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ADVANCED TECHNIQUES FOR DETERMINING LONG TERM COMPATIBILITY OF MATERIALS WITH PROPELLANTS

INTERIM REPORT D180-14839-1 JUNE 1972

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Prepared For

*The Jet Propulsion Laboratory
Pasadena, California 91103*

Under

*National Aeronautics And Space
Administration*

Contract

NAS7-789

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by

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FOREWORD

The work in this program was performed at The Boeing Company, in Seattle, Washington, under NASA Contract NAS7-789 during the period August 1, 1970 through June 15, 1972. The program was administered under the direction of the technical manager, Mr. Louis R. Toth of the Jet Propulsion Laboratory, Pasadena, California.

The project was managed at The Boeing Company by Mr. James R. O'Brien of Aero/Propulsion Research in the Research and Engineering Division. The technical effort was led by Dr. R. L. Green.

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1.0 SUMMARY

The search for advanced measurement techniques for determining long term compatibility of materials with propellants was conducted in several parts. A comprehensive survey of the existing measurement and testing technology for determining material-propellant interactions was performed. Selections were made from those existing techniques which were determined could meet or be made to meet the requirements. Areas of refinement or changes were recommended for improvement of others. Investigations were also performed to determine the feasibility and advantages of developing and using new techniques to achieve significant improvements over existing ones.

Complete technical demonstrations of four techniques were conducted through laboratory test programs. Demonstration of the radioactive tracer technique confirmed that it truly met the requirements of sensitivity and utility. Valuable data were generated concerning the interaction of hydrazine with Type 304 corrosion resistant steel.

Demonstration of a related technique, dry activation (neutron) analysis, pointed out some areas of weakness and some possible areas for refinement and improvement. The basic technique was shown to be very sensitive in determining subtle interaction between 6061 aluminum and liquid oxygen difluoride.

The palladium foil hydrogen analyzer was shown to provide information in a very short time concerning the relative reaction of diborane on the surface of 304 steel, 6061 aluminum, and 6Al-4V titanium. Very small amounts of hydrogen build-up from the diborane were noted, but conventional pressure measuring instruments would not have shown any pressure rise. The palladium foil hydrogen analyzer was noted to be rather specialized in application, but was considered a valuable contribution nevertheless.

Perhaps the most interesting demonstration was that of the new technique, the volatile metal chelate analysis. Rivaling the neutron activation analysis in terms of sensitivity and specificity, the volatile metal chelate technique was fully demonstrated using material

remaining from the three previous experiments. Agreement was considered quite good with previous measurements, considering the state of development of the technique. Being relatively new, this technique needs additional study to place it on par with other analytical procedures that have been used in the past.

In addition to the above techniques, atomic absorption spectroscopy was considered to meet the program requirements but was not demonstrated.

It was concluded that there are techniques available to predict the performance of material-propellant pairs for the long term from short term data, with a high level of confidence.

2.0 INTRODUCTION

The problem of material and propellant compatibility has concerned scientists and engineers for many years, but it is only recently that some of the more subtle and long-term effects of incompatibility have been recognized. For example, a few years ago an iron concentration in the propellant N_2O_4 of only 1 part per million by weight would have been considered insignificant. Now it is well established that such a concentration will produce the phenomenon of flow decay under the proper conditions and that such concentrations are normally present in N_2O_4 as the result of propellant - material interactions.

As deep space probe missions become longer, the question of long term compatibility becomes critical. To be certain that combinations of material and propellant are completely compatible for periods up to 15 years requires measurements and testing techniques more advanced than those in current use. Obviously the engineer cannot wait for the results of a 15 year test program before designing the components of the propulsion system. What is required, then, is an array of sensitive measurement techniques which can be applied to analysis of a given material-propellant combination for a short test period (e.g., about one month) and which can produce data on interaction rates which can be reliably extended or extrapolated to 15 years.

2.1 PROGRAM OBJECTIVES

The objective of this effort was to advance the art of techniques for qualifying materials and propellants used on chemical liquid propulsion feed systems required for unmanned space exploration vehicles. The materials were to be used with earth storable and space storable propellants at pressures up to 1000 psi and operate reliably in the space environment for long periods of up to fifteen years but on an intermittent duty cycle basis; for example, one or more duty cycles per year during the mission life.

The techniques developed to meet the objectives were required to yield data in a much shorter time than the mission life. Conceivably they would be capable of predictions of material-propellant functional

performance on only a relative basis. Accurate compatibility could be assigned by means of extremely sensitive measurements of the malefic effects of the propellant on the material, and conversely the effects of the exposure on the propellant. The words "materials and compatibility" were taken here in the broadest sense such as to include: source, processing, flight type usage, etc.

The scope of the work included analyses, design, feasibility experimentation, and technical demonstration.

Materials considered were related to the following liquid propulsion feed system functions:

- a. Flow shut off valves
- b. Isolation type valves
- c. Flow metering or throttling devices
- d. Regulators for cold gases
- e. Regulators for hot gases
- f. Vent or relief valves
- g. Fill or service valves
- h. Filters
- i. Tankage and propellant acquisition devices
- j. Lines and service connections

Primary emphasis was given to the propellants hydrazine, diborane and oxygen difluoride. Other propellants also considered were FLOX, liquid fluorine, monomethylhydrazine and nitrogen tetroxide.

2.2 SPECIFIC TASKS

2.2.1 Existing Technology Survey

A comprehensive survey was performed of the existing technology of methods, measurements, and testing techniques for qualifying liquid propulsion material-propellant combinations for spacecraft applications. Those which, as currently practiced, would contribute and provide meaningful results towards determining material-propellant compatibility,

performance, and reliability for long mission durations of up to fifteen (15) years in the space and planetary environments within the solar system were identified.

2.2.2 Evaluation of Existing Technology

After completion of the survey, a critical evaluation of the existing techniques was made to determine if any of them could be refined sufficiently to meet the requirements. Areas of improvement were noted.

2.2.3 Development of New Technology

Part of the program effort was devoted to investigating the feasibility and advantages of developing and utilizing new methods to achieve significant improvements over existing ones. Areas requiring technology advancement were also defined.

2.2.4 Experimental Demonstration

A complete experimental demonstration of one or more of the techniques identified in the preceding tasks was accomplished. A test program was conducted that gave reliable evidence that the information obtained was directly correlatable with extended periods of time, and gave reliable evidence that the basic program requirements were met assuring satisfactory spacecraft service.

In addition to the above, the sensitivity and practical utility of the volatile metal chelate technique with respect to analysis of trace metals in oxygen difluoride, hydrazine, and diborane liquid propellants was demonstrated.

Determination of long term compatibility between materials and propellant was most logically treated in two parts, namely; (1) the effect of materials on the propellant during long-term storage and (2) the effect of the propellant on materials during long-term storage or intermittent exposure over a long time period. A study of both parts, which required a comprehensive evaluation of the entire materials compatibility interface, was a formidable undertaking, and a review of the overall study requirements indicated that reasonable constraints must be imposed on the scope of the technical effort. Thus emphasis was placed on those measurement and testing techniques that apply to determining the effect of materials on the propellant. The treatment of the measurement and testing techniques applicable to determining the effect that the

propellant has on materials was limited to the survey of existing and advanced technologies. A preliminary evaluation of those techniques was also provided. By concentrating the technical effort on the aspects of the problem concerning the propellant, a positive and meaningful program was evolved which met the objectives.

3.0 EXISTING TECHNOLOGY SURVEY

3.1 INTRODUCTION

3.1.1 Definitions

During the course of this study the following definitions were used:

Measurement Technique - An operation or sequence of operations that results in the measurement of some physical or chemical quantity.

Testing Technique - A sequence of operations that involves one or more measurement techniques under a specified set of conditions and order.

Method - An overall approach to the solution of a problem, including testing techniques, and interpretation and presentation of data.

3.1.2 Survey

A survey was conducted to identify those measurement and testing techniques which are currently used to qualify liquid propulsion feed system material-propellant combinations for spacecraft applications. A literature search was performed to identify those techniques which as currently practiced (though not necessarily utilized) would contribute meaningful information towards determining long term material-propellant compatibility, performance, and reliability. In this work, long term was taken to mean durations of up to fifteen years. Although the study emphasized aluminum alloys, titanium alloys, and 300-series stainless steels, other metallics were considered when information was readily available.

The propellants involved in the survey included the following:

- a. Hydrazine
- b. Oxygen difluoride
- c. Diborane
- d. Liquid fluoroine
- e. Nitrogen tetroxide
- f. Monomethylhydrazine

Again, techniques involving the qualification of materials in contact with other reactive liquids were considered when available.

3.2 FACILITIES

The resources of the Information Group of the Boeing Aerospace Technical Library were utilized extensively during this survey. As experts in the science of information collection, they conserved considerable time and energy in the development of the following bibliographies:

1. Non-destructive Testing Techniques
2. Effects of Diborane, Liquid Fluorine, Mixed Hydrazines, Monomethylhydrazine, Nitrogen Tetroxide and Oxygen Difluoride on Aluminum, Titanium and Stainless Steel.
3. Propellant and Oxidizer Effects
4. Techniques for Metal Analysis
5. Micro and Ultramicro Analytical Techniques

Additionally, the following bibliographies were compiled from computer searches of the NASA Linear File Search System:

1. Non-destructive Testing of Propulsion Systems
2. Propellant Effects on Metals
3. Metal Analysis

Application to the Defense Documentation Center, Alexandria, Virginia resulted in the following classified bibliographies:

1. Report on Hydrazine Compatibility with Materials (U), (Confidential).
2. Storage Life Capabilities of Various Components and Sub-assemblies in Contact with Monomethylhydrazine and Nitrogen Tetroxide (U), (Confidential).
3. Spacecraft Fuel Systems Compatibility Studies (U), No. 044999 (Confidential).
4. Sensitive Techniques (U), No. A46166 (Secret).

5. Compatibility of Selected Liquid Propellants with Al, Ti, and Stainless Steel (U), No. 045408, (Confidential).

All of the above bibliographies remain on file at The Boeing Company for future reference.

Finally, in addition to the above searches, the Chemical Abstracts, Liquid Propellant Information Agency Abstracts, and Chemical Propulsion Information Abstracts were consulted on various selected subjects.

In an effort to consider unreported research and development information, questionnaires were sent to 114 government and industry organizations throughout the country. The questionnaire, shown in Figure 3-1, requested information concerning measurement or testing techniques which could determine subtle effects of interaction between metallic materials and liquid rocket propellants.

3.3 RESULTS

The criteria for the consideration of any measurement technique were the following:

1. The technique must be capable of measuring changes leading to differences of the order of 10^{-6} on the surface or in the bulk of the material and/or concentrations of metals in the liquid of the order of 10^{-6} grams per milliliter or less.
2. The technique should be capable of identifying specific elements and/or compounds.
3. The technique should be versatile such that a wide range of changes or effects can be identified by one method.
4. The technique should give short term data that can be used to make reliable estimates of the extent of interaction over the long term.

The majority of the work encountered in the survey was composed of corrosion studies. Studies of general corrosion prior to 1967 were largely reviewed in one publication concerned with material-propellant

QUESTIONNAIRE

1. Measurement or testing techniques which could be used to determine subtle or tenuous interaction between metallic materials and liquid rocket propellants (such as pin-holes or metal dissolution) are being pursued. Do you have knowledge of such techniques? ☐ Yes ☐ No

If yes, please describe _____

2. What is the limit of detection of the technique? _____
3. In your opinion, can this technique be used to extrapolate short term data (of a few weeks or months) to reliable estimates of interaction over 15 years? _____

4. Is this technique:

Commercially Available	Proprietary	Patented	Patent Applied	Public Domain
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

5. If you are currently researching a new technique which may benefit the industry or NASA, would you describe your current work? _____

6. ☐ Description of the technique is not amenable to this questionnaire or, I have other information, please call me on _____

Name of person answering questionnaire _____
Title _____

If additional space is required, please use another page. Please return by November 30, 1970 to:

The Boeing Company
Aerospace Group
P.O. Box 3999
Seattle, Washington 98124

Attention: R. L. Green - Mail Stop 8C-76

Figure 3-1 Questionnaire Sent to Government and Industry

compatibility (1)*. A considerable proportion of the remaining compatibility study references were directed to investigations of stress corrosion.

In both the general corrosion and stress corrosion investigations, conventional approaches were used for assessing whether or not interactions were occurring between the alloys and the propellants. The extent of general corrosion was estimated from surface appearances (macroscopic or microscopic), weight changes, hardness and the appearance and analysis of corrosion products (1-17). The stress corrosion studies utilized the standard procedure of loading to a certain percentage of the yield point or plastically deforming (e.g., U-bend specimens), exposing to the selected environment, and examining for cracks or recording failures.

The degradation of the propellant was largely estimated by determination of pressure build-up or visual observation of bubbles (3-5, 12).

These approaches were not considered capable of satisfying the major objectives of this investigation. Techniques identified during the literature search which showed promise of fulfilling these requirements are the following:

1. Photoemission Electron Microscopy (Exo-electron emission).
2. Rutherford Scattering Spectroscopy (α particle recoil).
3. Secondary (Auger) Electron Spectroscopy
4. Acoustic Emission Spectroscopy
5. Electrography
6. Ultrasonic Surface Interferometry
7. Eddy Current Testing
8. Holographic Interferometry
9. Electron Microprobe Analyzer

* Numbers in parentheses refer to references in Section 9.0.

10. Surface Impedance Changes
11. Palladium Foil Hydrogen Analysis
12. Micro-Oxygen Analysis (Hersch Cell)
13. Nuclear Activation Analysis
14. Atomic Absorption Spectroscopy
15. Electrogravimetric Analysis

The first ten techniques apply to the analysis of surface or solids; the latter five apply to the analyses of liquids (and in some cases to solids). The majority have been used in surface and materials research, but according to current reports, they are not used routinely for material-propellant qualification with the possible exception of atomic absorption spectroscopy.

A summary of the techniques surveyed is presented in Table 3-1. Brief comments on each technique, together with data (when it exists) concerning sensitivity, accuracy and precision are presented below.

Photoemission Electron Microscopy (18-21)

The photoemission microscope is ideally suited for imaging structures in plane surfaces. The principle of operation is as follows: The surface of a compact specimen is illuminated by means of an intense ultraviolet source using quartz optics. The ultraviolet light produces electrons from the surface (photoeffect), which are accelerated by an electric field of 100 kV/cm between the surface and the anode. After passing through the anode diaphragm, the electrons enter a normal three-stage magnetic electron microscope with luminescent observation screen and photographic devices. The direct electron optical magnification is variable between 100 and 10,000. The resolution limit is 150 to 300 Angstroms (\AA), depending upon the material.

Image production in the photoemission electron microscope is based on the photoeffect and the contrast is determined essentially by the work function for metal being observed. The work function varies from material to material and therefore results in strong material contrast. This sensitivity allows one to differentiate between substances and phases. The technique is very sensitive to surface coatings and is not tied to any relief pattern. Photoemission is especially suitable for

Table 3-1 SURVEY SUMMARY

<u>Technique</u>	<u>Application</u>	<u>Limits</u>
Photoemission Electron Microscopy	Surface magnification, surface coatings	10,000 x
Rutherford Scattering Spectroscopy	Chemical analysis of surface	Top 1 to 100 μ
Auger Electron Spectroscopy	Chemical analysis of surface, surface, light elements	First atomic layers
Acoustic Emission Spectroscopy	Plastic deformation, predicts failure	
Electrography	Detects flaws and cracks	
Ultrasonic Surface Interferometry	Detects phase, topographic and hardness changes	10 - 20 mils depth
Eddy Current	Detects flaws and corrosion	
Holographic Interferometry	Detects differences in density, allows time-lapse recording of chemical reaction	
Electron Microprobe	Determines composition of thin oxide films	Film thickness 0.1 to 0.4 μ
Surface Impedance	Determines relative oxide film thickness and presence of pin holes	
Palladium Foil Hydrogen Analyzer	Detects hydrogen	10 x 10 ⁻⁹ grams

Table 3-1 (Cont.)

<u>Technique</u>	<u>Application</u>	<u>Limits</u>
Micro-Oxygen Analysis	Detects oxygen	10^{-8} to 10^{-7} grams
Nuclear Activation Analysis	Detects most elements	Variable
Atomic Absorption Spectroscopy	Detects many elements	Variable
Electrogravimetric Analysis	Detects many elements	Cd, .005 ppm

the imaging of a plane surface, since in most cases the depth of electron-emission, and therefore of information, is less than 100 Å.

Rutherford Scattering Spectroscopy (22-24)

Chemical analysis can be made by use of large-angle scattering of heavy, charged particles. Rutherford scattering of charged particles from the heavier elements and nuclear scattering and (α , p) reactions from the light elements result in energy spectra that are characteristic of the nucleus being bombarded.

Several instruments have been designed around this principle, among which are the JPL instrument for lunar surface analysis and an instrument designed and used several years ago at The Boeing Company. All of them use a radioactive nuclide such as Cm²⁴² or Am²⁴¹ as a source of monoenergetic alpha particles. The energy distribution of backscattered alpha particles is measured with semi-conductor detectors. Other detectors, shielded by gold foils to eliminate α particles, register protons from (α , p) reactions.

The method is particularly well suited for the detection and analysis of contaminants or reactants chemically attached to solid substrates. The analysis of solids (the top 1 to 100 microns) is best conducted in vacuum. The analysis is nondestructive and it determines elements present. Currently, the technique does not have the required sensitivity, but with the use of high quality preamplifiers and pulse height analyzers of 1000+ channels, the sensitivity and accuracy can be improved sufficiently to measure subtle chemical changes on metal surfaces.

Secondary (Auger) Electron Spectroscopy (25-26)

The technique is comparable to Rutherford scattering but instead of surface bombardment with α particles, electron bombardment is used. To analyze a material, a solid sample is bombarded in a vacuum with a stream of relatively low-energy electrons. The sample emits secondary electrons (Auger electrons). The electron emissions are recorded according to their various energy levels. The Auger electrons possess a characteristic amount of energy depending upon the atom from which they originate. Thus an analysis of the Auger electrons can reveal impurities and chemical changes at the surface the sample being tested.

This is reportedly the most sensitive technique available at the present time for surface analysis. Atoms at, or several atomic layers below, a material surface can be detected. The technique is particularly well suited for detecting and identifying surface atoms of the lighter elements such as lithium, beryllium, boron, carbon, sulfur, and oxygen. As a result, the method has merit in applications to determine subtle effects of metal reactions with fuels and oxidizers containing these elements.

Acoustic Emission Spectroscopy (27-29)

The acoustic emission phenomenon can be used as an extremely sensitive tool for the nondestructive evaluation of metals. Test techniques have been developed for measuring extremely low-level acoustic emission and reportedly is able to indicate impending failure or extrapolation of short-term use time, to time of failure. At the present, the acoustic technique provides qualitative information in the plastic deformation range. But while it does not provide quantitative information, it does sense plastic deformation wherever it may occur in the sample.

The technique uses piezoelectric transducers attached to the specimen being tested. Sound emitted by the specimen in the stressed condition is detected and amplified $10^6 - 10^7$ times for measurement.

The effect has been studied under Air Force and NASA sponsorship. The experiments have shown that various seamless steel cylinders behave differently. Tanks without cracks or flaws when tested in their as-received condition gave very small amplitude emission with increasing stress and deformation until just prior to failure. However, the behavior of tanks with cracks was quite unique. Premature fluctuations in emission amplitude were observed almost from onset of the test. The emissions were caused by intense local plastic yielding due to the flaws and cracks. Refining of the technique promises a method for predicting usable life (long time prediction) of propellant and oxidizer tanks, especially when filled.

Electrography (30-32)

Electrography is a method for reproducing surface characteristics of objects in order to detect minute flaws and cracks not detectable by less sensitive methods such as penetrant inspection.

The method produces colored products when an electric current flows from a test specimen to a gelatine coated paper soaked in a suitable electrolyte. Brilliant colored products are produced by 50 micrograms of most metals.

The technique has several advantages. It furnishes a permanent record of surface flaws. It is nondestructive and it is sensitive enough to detect most materials in the microgram range.

Ultrasonic Surface Interferometry (33-35)

Ultrasonic surface interferometry is a variation of ultrasonic testing that takes advantage of wave reinforcement and cancellation when the wave is reflected from a material surface at an angle.

It is claimed that ultrasonic-surface interferometry will show minute changes such as phase, topographic, and hardness below the ability of other metallurgical techniques. It applies to surface layers to 10-20 mils. depth.

Eddy Current Testing (36-37)

Eddy current testing, a relatively new nondestructive technique, has great potential but is limited to regularly shaped objects. Its application to liquid propellant systems is probably limited to experiments on pipes.

The principle is based on the fact that induced currents in electrical conductors are affected by flaws in the conductor. A coil or point probe carrying high-frequency alternating current is used to generate eddy or induced currents in the conductor specimen. By Lenz' law there is a magnetic field associated with the induced currents. Flaws, as well as variations in mechanical, chemical, or physical properties, cause resistivity changes in the specimen. The resistivity, in turn, affects the induced current and the resultant magnetic field. Measurement of distortions in the magnetic field is the basis for detecting flaws. In addition to minute flaw detection, the technique has been used to detect the presence of corrosion. No quantitative measure of corrosion has been reported.

Holographic Interferometry (38)

References (1) and (2) discuss the advantages of holographic interferometry for general corrosion testing and (38) details the application of holography to stress corrosion investigations at the University of Michigan's Willow Run Laboratories. Interference patterns result when two light beams with only minute differences are superimposed. A hologram is a photographic recording of those interference patterns. The attractive feature of the holographic interferometric technique is that one of the light beams may be stored so that the test and comparison beams are separated in time. This allows observation of the real time behavior of an object in a manner that cannot be accomplished otherwise. A time-lapse or moving picture record can also show chemical reactions in progress. TRW Systems Group has applied this technique to the study of the corrosion of 1020 cold-rolled steel in concentrated nitric acid ⁽²⁾. In this case, vigorous reaction was observed with reaction products clearly seen streaming downward from the metal surface. Whether or not the technique is sensitive enough to detect subtle changes remains to be seen. In a general consideration of sensitive analytical techniques, the holographic method should definitely be included among those that show promise of great sensitivity. From the discussions read in this survey, however, it does not appear that the holographic technique will be competitive with others that are available at this time.

Electron Microprobe Analyzer (39)

Another method of analysis applicable in studies involving surface interactions is the use of the electron microprobe analyzer for determining the composition of very thin oxide films. These films, ranging in thickness from 0.1 to 0.4 μ , are chemically removed from the surface following the application of a surface coating of carbon. The stripping solution used is generally a methanol-iodine mix. After the surface film is removed, it is analyzed using the electron microprobe.

Following a methanol wash and an immersion in acetone, fragments of the film are caught on electron microscope grids. Colloidal graphite and alcohol are used to fix the grid to the microprobe holder, then 1000 Å of carbon is evaporated onto the surface of the overall combination to assist in retention of the grid and to alleviate surface charging.

This analytical approach seems well worth investigating since the surface extraction technique can be used also with aluminum alloys and titanium alloys. Indications are that the approach can also be used for thin fluoride films. There seems to be little problem to be anticipated in removal of thin fluoride films which would form in LF_2 environment. However, as with all wet extraction techniques, the possibilities of intermediate chemical reactions during the extraction process must be considered.

Surface Impedance Changes (40-41)

Surfaces of aluminum, titanium, stainless steel and most other metals are normally well coated with an oxide film 20 to 25 Å thick because of their interaction with an oxidizing atmosphere. The oxide film has dielectric properties which can be used to establish film thickness and film integrity. When the metal and its oxide film are combined with a proper conductor, an electrical circuit can be formed which will enable one to measure the impedance of the surface film. The impedance can be divided into a capacitance and dissipative terms which give information about the film thickness and the presence of pin holes in the film. With the proper experimental techniques it should be possible to follow the rate of change of the oxide film thickness with time while in a propellant environment.

The impedance change measurement technique has proved successful in its application to very thin films of hydrated oxides or hydroxides on aluminum alloys and would appear to have general applicability to titanium and stainless steel alloys. This method would appear to be especially useful as a scanning technique.

Palladium Foil Hydrogen Analyzer (42-44)

The palladium foil hydrogen analyzer determines hydrogen quantitatively by separating it from other gases by means of diffusion through a heated palladium foil. Such a foil permits the passage of hydrogen, but is impervious to all other gases. It is sealed to an ion-getter pump, which responds to the presence of hydrogen by pumping and removing it. The current produced in pumping is proportional to the hydrogen sensed by the pump. An appropriate calibration correlates the amount of hydrogen to the pumping current.

The apparatus has been used to determine hydrogen in metals. An intense heat source is used to evaporate the dissolved hydrogen from the material surface. In conjunction with a laser beam, it has been used to measure hydrogen concentrations down to 10 parts per billion by weight (ppb) in small spots on metal surfaces. Such a device could be applied to detecting very small degradations of hydrogen-containing propellants by measuring the hydrogen gas evolved. The method is essentially non-destructive.

The technique has the required sensitivity to detect and measure subtle effects in hydrogen-containing propellants and materials. The method is sensitive to 10 nanograms of hydrogen (10-100 ppb for samples used). The precision is ± 30 nanograms of hydrogen. Accuracy is estimated to be ± 60 nanograms of hydrogen.

Micro Oxygen Analysis (Hersch Cell) (45-46)

The Hersch cell has been used as a detector in gas chromatography instruments and to determine oxygen dissolved in metals such as 4340 steel, aluminum and titanium alloys. The device consists of a silver cathode and a lead anode in contact with an electrolyte containing hydroxyl ions. By electrochemical action oxygen is reduced at the cathode and results in the generation of an electrical current which is proportional to the amount of oxygen present.

The cell can be used to determine oxygen liberated in the surface-induced decomposition of oxygen-containing propellants and, conversely, to determine oxygen absorbed or reacted with container materials.

The cell is extremely sensitive - approaching that of a helium ionization detector. It is capable of detecting less than 10^{-5} scc of oxygen under ideal conditions, and is specific for oxygen. The Boeing Company has used the technique to measure oxygen in the presence of hydrogen in an argon gas stream. Precision of results for short periods of time has been reported to be better than 1% standard deviation.

Nuclear Activation Analysis (47)

The term nuclear activation refers to the process that is used to render stable elements radioactive so that they may be identified and

measured. For some elements, nuclear activation analysis is the most sensitive method of analysis known. The nuclear activation technique is well suited to following reactions with time or to following the movement of chemical species within a system.

The technique is particularly suited for the sensitive and accurate determination of a large number of elements which are not conveniently determined by standard methods of trace analysis. In contrast to chemical analyses, the principal limitations of the technique are due to the nuclear properties of an element and not its chemistry. The sensitivity of the technique is a function of the manner and length of irradiation (activation) and the element in question. The detection limit can be .001 to .00001 ppm for many elements of interest with only moderate irradiation levels.

Atomic Absorption Spectroscopy (48)

Atomic absorption is precise, easy to use, and has good detection limits. In the analysis, the sample is atomized in a high temperature flame which breaks the chemical bonds in the molecules of the sample, enabling individual atoms to float freely in the flame. In this state, the atoms can absorb ultraviolet or visible radiation. The wavelength bands in which each element absorbs are very narrow, and are specific.

In order to determine the concentration of aluminum, for example, light of the same wavelength as the absorption is passed through the flame. The light source is generally a hollow-cathode lamp with the cathode containing the element of interest, in this case aluminum.

A certain amount of the light passing through the flame will be absorbed, depending on the concentration of aluminum in the sample. The amount of absorption is measured by a spectrophotometer which compares the original light beam to the test beam. Most instruments can be set to indicate their results directly in concentration values.

Some detection limits for a research grade atomic absorption spectrophotometer are: aluminum, 0.03 $\mu\text{g/ml}$; iron, 0.01 $\mu\text{g/ml}$; and titanium, 0.09 $\mu\text{g/ml}$ (48).

Electrogravimetric Analysis

Electrogravimetric analysis, or electrodeposition, is normally applicable to the determination of metal concentrations greater than about .001 molar (M). The lower limit of conventional electrodeposition is primarily imposed by the difficulties in measuring small mass changes with an analytical balance. Perhaps more significant is the fact that long times are required for complete deposition from dilute solutions in which electrical currents will be relatively small. A new technique which largely overcomes these problems, involves electrodeposition of metals onto gold electrode surfaces of a conventional quartz piezoelectric crystal causing small mass changes to the unit. Incorporation of the unit into an oscillator circuit and measurement of the change in frequency of the crystal due to the increase in mass allows a highly sensitive indication of solution concentrations down to the micromolar level. Currently, in the case of cadmium, analyses have extended from 5×10^{-4} M to 5×10^{-8} M. The reported work has been done using aqueous electrolytes. Extension to other liquids is unknown.

3.4 RESULTS OF THE QUESTIONNAIRE

Questionnaires were sent to 114 individuals in government and industry seeking information concerning measurement or testing techniques which could detect subtle or tenuous interaction between metallic materials and liquid rocket propellants. A total of 52 replies were received; thirty percent of these were affirmative or had useful information to offer. The remainder indicated that they did not know of techniques that would satisfy the requirements. The results from the questionnaire are summarized in Table 3.2.

It was noted that the majority of suggestions were concerned with surface measurements. While it was realized that there are a large number of powerful surface evaluation techniques available, it was the basic premise of this work to consider them at a low level of effort. The techniques which pertain to solutions have been discussed above.

Table 3-2 RESULTS OF THE QUESTIONNAIRE

Method Suggested	Applies to Surfaces	Applies to Propellant or Solutions	Number of Times Suggested
Electron microprobe	x		1
Electron microprobe		x	3
Electrochemical techniques	x	x	1
Holographic interferometry	x		1
Eddy current	x		1
Magnetic perturbation	x		1
Electric current injection	x		1
Barkhausen noise	x		1
Ultrasonic-surface interferometry	x		1
Radioactive penetrants	x		1
Atomic Absorption Spectroscopy		x	2
Surface impedance	x		1
ESCA* and Auger Spectroscopy	x		1

*Electron Spectroscopy Chemical Analysis

4.0 EVALUATION OF EXISTING TECHNIQUES

4.1 INTRODUCTION

Techniques have been identified which as currently practiced would provide information towards determining material-propellant compatibility. These techniques have been thoroughly examined to determine if there are areas where refinement or improvement could be made. The techniques investigated were:

1. Atomic Absorption Spectroscopy
2. Electrochemical Methods
3. Nuclear Activation Analysis
4. Electrogravimetric Analysis
5. Palladium Foil Hydrogen Analyzer
6. Hersch Oxygen Cell
7. Holographic Interferometry

4.2 REVIEW

Atomic Absorption Spectroscopy

The technique of atomic absorption spectroscopy (AAS) has been critically reviewed and promises to fulfill the requirements for a very sensitive technique. AAS has been found to be a simple, inexpensive, and accurate technique that is applicable to many metals of interest. It is limited, however, when determining those elements which form refractory oxides such as aluminum and titanium. These high melting oxides limit the number of free atoms in the air-acetylene flame which produce the characteristic absorption. The recent use of a nitrous oxide-acetylene flame with its higher flame temperature has extended the limit of detectability for this class of elements.

A nontrivial problem exists when it is necessary to introduce a cryogenic or reactive propellant into the flame of the spectrometer. A procedure of evaporating the cryogen or propellant, dissolving the residue in a suitable solvent, and then using the normal techniques would be

required. Such procedures are generally subject to several sources of error. Among these are: impure reagents, additional contact with glassware, and volatilization of low boiling trace constituents during the evaporation process. The Perkin-Elmer spectrometers have an accessory called a Sampling BoatTM which may be applicable for this type of analysis. With such an accessory, the sample is evaporated in the boat and the boat is inserted directly into the flame.

Modifications to the AAS technique include a number of advanced atomization techniques which have been reported in the literature: electrically heated graphite crucible, RF plasma torch, pulsed laser, DC arc discharge, electron bombardment, and monochromated xenon arc. These atomization techniques produce stable, homogeneous, high temperature atomic sources from samples and thereby increase sensitivity. Each has its own merits and all need substantial development work to prove their value. Another area where improvement can be made is the radiation source of the AAS. The hollow-cathode discharge tube is currently the most popular source of visible radiation but other sources may prove to be more suitable. Two sources which have shown promise are microwave-excited, electrodeless tubes and the high frequency plasma torch.

The AAS method has been continually improved during the last five years, and refinements in commercial instruments allows it to qualify as an available technique to determine compatibility of materials with propellants which require one microgram (μg) sensitivity or lower. Some detection limits are given below.

Table 4-1 DETECTION LIMITS OF APPLICABLE METALS USING
ATOMIC ABSORPTION SPECTROMETRY

Metal	Detection Limit, $\mu\text{g/ml}$	
	Massman, 1965 ⁽⁵⁰⁾	Perkin-Elmer 503, 1970 ⁽⁴⁸⁾
Al	9	.03*
Cr	.2	.003
Cu	.1	.002
Fe	.1	.01
Mn	.06	.002
Mo	.7	.03*
Ni	.3	.01
Ti	-	.01
V	-	.09*
Zn	.02	.002
Zr	-	5.*

* Nitrous oxide/acetylene flame

Electrochemical Techniques

Electrochemical measuring techniques have been used for years in determining trace quantities of certain elements. These methods in general are used with aqueous solutions and rely upon the concept of electrochemical half-cells. The subject of electrochemistry is exceedingly broad, since all chemical interactions are fundamentally electrical in nature. Electrochemical measuring techniques encompass a large number of methods including polarography (of which there is a multitude of variations), coulometry, potentiometry, stripping analysis, and conductance. Some of these methods apply only to special situations or to

specific elements. A comparison of the sensitivities of these analytical methods is revealing, however. The sensitivity limit is defined as the lowest concentration at which a determination can be made with a relative precision of 10% in the presence of a large concentration of a major constituent. A comparison of various electroanalytical methods is given in Table 4-2.

Table 4-2 QUANTITATIVE SENSITIVITY LIMITS OF SOME ELECTROANALYTICAL METHODS

Sensitivity limit, Moles	
$10^{-4} - 10^{-5}$	AC polarography, Chronopotentiometry, Thin layer coulometry, Potentiometry with metal-specific glass or membrane electrodes.
$10^{-5} - 10^{-6}$	Classical polarography, Coulometry at controlled potential, Chronocoulometry, Precision nullpoint, potentiometry
$10^{-6} - 10^{-7}$	Tast polarography, Derivative polarography, Square wave polarography, Second harmonic AC polarography, Phase-sensitive AC polarography, Linear sweep voltammetry, Staircase voltammetry, Derivative voltammetry, Coulostatic analysis, Chemical stripping analysis.
$10^{-7} - 10^{-8}$	Pulse polarography, RF polarography, Coulometric titrations, Amperometry with rotating electrodes, conductivity (aqueous)
$10^{-7} - 10^{-9}$	Anodic stripping with hanging mercury drop electrodes
$10^{-9} - 10^{-10}$	Anodic stripping with thin film electrodes or solid electrodes

The outstanding modification in the field of electroanalysis is the technique of anodic stripping analysis with thin film electrodes. This method involves the reduction of the trace metal ions in an aqueous solution on a thin mercury film supported on a graphite electrode. When all the metal ions have been reduced the electrolysis is reversed and scanned anodically. Because of the extreme thinness of the mercury film the reduced metal is held essentially at the surface of the mercury. A

current versus potential curve shows peaks for the oxidation of each metal with peak height being related to concentration. Each metal oxidizes at a specific potential providing a means of identifying an unknown. A mixture of trace metal results in an "anodic stripping trace" that resembles a chromatogram. This technique can be applied to trace metal ions at levels as low as 10^{-9} to 10^{-11} grams/ml.

Nuclear Activation Analysis

The general principles of nuclear activation analysis have not changed since they were set out in the late 1940's and early 1950's. The basic relation for activation is:

$$A = f \frac{\sigma \phi W}{M} (1 - e^{-\lambda t}) \times 6.02 \times 10^{23}.$$

where

A = induced activity in disintegrations/sec at the end of irradiation.

ϕ = flux of "particles" used in the irradiation, in number/cm²/sec

σ = the activation cross section for the nuclear reaction concerned, in cm².

W = weight of element irradiated, in grams

f = fractional abundance of the particular isotope of the element

M = atomic weight of that element.

λ = the decay constant of the induced radionuclide, in sec⁻¹

t = irradiation time, in seconds

After irradiation, the induced activity will decay with a characteristic half life, falling by a factor of two in each half life period. The sensitivity of the technique is directly proportional to the activity of the constituent. In practice there are interferences which reduce the utility of the technique, e.g., background radiation and closely-spaced disintegration energies. These difficulties can be overcome with certain techniques and some of the new developments in activation analysis are oriented toward solving them. For example, if a disintegrating nuclide emits particles of different energy simultaneously, the detector can be set up

to accept those energy levels only when they occur simultaneously. This practice, called coincidence counting, virtually eliminates background. Also, a new generation of solid-state detector devices is now enabling much higher resolution of particle energies. Thus, closely-spaced disintegration energies may now be separated.

As applied to analysis of trace contaminants in liquid propellants, nuclear activation analysis presents some interesting advantages. If the liquids are cryogenic, the propellant may be evaporated, leaving the contaminants as a residue. The residue may then be activated and the analysis completed. No redissolving with another solvent is necessary. This new technique has been explored recently under another NASA contract (NAS7-779). Also, the level of contaminant buildup may be monitored continuously if the contaminating material has been previously activated, and one may be absolutely certain of the source of the contaminants. This technique can be quite sensitive for most elements of interest. Furthermore, most alloys will generally contain some element which has a high activity and which can serve as an indicator of contamination buildup. Some detection limits are shown in Table 4-3.

Table 4-3 DETECTION LIMITS OF APPLICABLE METALS USING
NUCLEAR ACTIVATION ANALYSIS

Metal	1 hour Activation	10 hours Activation
	ug	ug
Al	.001	.001
Cr	.1	.01
Cu	.0001	.0001
Fe	4.	.4
Mn	.000004	.000004
Mo	.01	.001
Ni	.004	.004
Ti	.01	.01
V	.001	.0001
Zn	1.	.1
Zr	.1	.01

Electrogravimetric Analysis

An improved method of electrogravimetric analysis has been reviewed, which involves the use of a gold-plated piezoelectric transducer upon which metallic components from an aqueous solution are electrolytically deposited. The change in mass of the transducer is determined to a high degree by an electronic oscillator-counting circuit. It has been determined that no current work is being done with the technique. As with the electrochemical methods, the technique has no application to propellants of low or negligible conductivity unless the contaminants are separated from the propellant and then dissolved in water.

A possible application of the technique would be to plate or otherwise attach the material or alloy of interest to the piezoelectric transducer and then determine weight gain or loss after immersion in the liquid propellant of interest. Without further study, however, it is not clear that this method would be superior to conventional microbalance techniques.

Palladium Foil Hydrogen Analyzer

The palladium foil hydrogen analyzer determines the presence of hydrogen in carrier gases by separating it from them by means of a palladium foil. The palladium foil permits the passage of hydrogen only. The palladium foil is sealed to an ion-getter pump which responds to the presence of hydrogen by pumping and removing it. The electric current produced in pumping is proportional to the amount of hydrogen passed through the palladium foil. Calibration of the ion-getter pump with known amounts of hydrogen enable quantitative analyses to be performed. The apparatus has been shown to have a sensitivity of 10 nanograms of hydrogen with a precision of ± 30 nanograms and an accuracy of ± 60 nanograms.

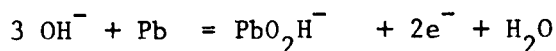
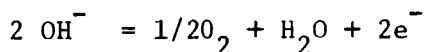
A review of this technique revealed that this is the most sensitive practical technique known for hydrogen. Yet the apparatus required to implement this method is so simple that it almost belies its true utility, especially when compared to such complex machines as the mass spectrometer.

The palladium foil hydrogen analyzer can be especially useful in following the reaction of diborane propellant with metal surfaces. Diborane slowly decomposes at temperatures above -20°C into hydrogen

gas and higher boranes. Practically all reactions that diborane undergoes with other chemical entities results in the liberation of hydrogen. It follows then, that interaction of diborane with metallic surfaces will usually result in hydrogen which, if measurable, could be detected with the palladium foil hydrogen analyzer.

Hersch Oxygen Cell

The Hersch cell relies on the electrochemical half-cell reactions



where the first reaction takes place at a silver electrode and the second reaction takes place at a lead electrode.

The cell is specific to oxygen and responds to its presence by producing an electromotive force or potential. As little as .00001 std. cc of oxygen will produce a measurable potential across the electrodes.

The basic chemistry is fixed by the half-cell reactions and therefore, unless a change in basic concept is made, no improvement in sensitivity is envisioned.

Improvements in design or geometry may result in increased stability or reproducibility. Various cell designs have been used but a simple one-tube arrangement with cotton separating the silver and lead electrodes seems to be satisfactory. One variation uses a lead rod which is wrapped with a layer of porous polyvinylchloride, on top of which is wound a layer of silver gauze. The electrolyte is a potassium hydroxide solution which wets the gauze. Another design uses a probe with a silver disk or button at the end and a lead ring concentric with the silver. The electrodes are molded in place with a plastic or epoxy. A piece of lens tissue maintains the electrolyte in contact with the electrodes and a 1.0 mil polyethylene membrane covers the end of the probe assembly. These designs may prove to have long term stability and give better than the 1% relative standard deviation currently available.

Holographic Interferometry

The holographic interferometry technique is in an early state of development. It is apparently capable of visibly indicating the

interaction between a liquid and a material. The detection limit (sensitivity) of the technique is not known. The interference fringes are, in part, a result of concentration gradients in the fluid. In order to correlate the appearance of the fringes with the concentration of material in the fluid, it would be necessary that a standard concentration gradient be set up or calibration be performed. TRW Systems Group is currently working on this concept to extend its detection sensitivity and determine the corrosion modes to which the technique can be applied.

In summary, the following techniques were judged as being capable of meeting the study requirements:

Atomic Absorption Spectroscopy

Anodic Stripping Electroanalysis

Nuclear Activation Analysis

Palladium Foil Hydrogen Analysis

The Palladium Foil Hydrogen Analysis technique and the Nuclear Activation Analysis (in both the radioactive tracer and the dry activation technique forms) were recommended for technical demonstration.

5.0 DEVELOPMENT OF NEW TECHNOLOGY

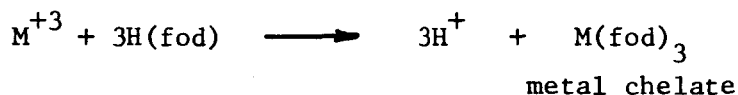
Examination of the possibility of utilizing and developing new technology to achieve significant improvements led to the considerations of the following techniques:

1. Volatile Metal Chelate
2. Surface Impedance
3. Nuclear Magnetic Resonance

The first one is a new technique which has very high sensitivity in metal analysis. The second, although dealing with the material surface rather than the propellant, shows real promise and may be developed to give qualification quickly on a relative basis. The third has been known for some time but it has not been developed for qualifying materials and its practical utility has not been demonstrated.

5.1 VOLATILE METAL CHELATE TECHNIQUE

The analysis of trace quantities of metals in liquid propellants resulting from material-propellant interaction can be accomplished by the use of powerful chelating agents such as fluorinated β -diketones. The chemical reaction playing the leading role in this analysis is



where H(fod) is 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione. The metal chelate formed has a relatively high volatility, which makes it possible to carry out an analysis using a mass spectrometer. The high sensitivity of the mass spectrometer plus the volatility of the high molecular weight (900-1000) metal chelate work together to produce a technique capable of detection of 10^{-12} grams of a number of elements.

Some initial experiments here have shown that the metal chelates were easy to prepare and that the analysis is straightforward. Mass spectra were obtained for several metal chelates.

The direct action of H(fod), on 6Al-4V titanium yielded the quantitative dissolution of the alloy. About 2×10^{-5} grams of the reaction product was used to produce a mass spectrum. The spectrum confirmed the presence of both Al(fod)_3 and Ti(fod)_3 defined by separate, unique mass-to-charge ratio peaks in the spectrum. Based on initial measurements, it was estimated that 10^{-12} grams of aluminum could be detected.

5.2 SURFACE IMPEDANCE TECHNIQUE

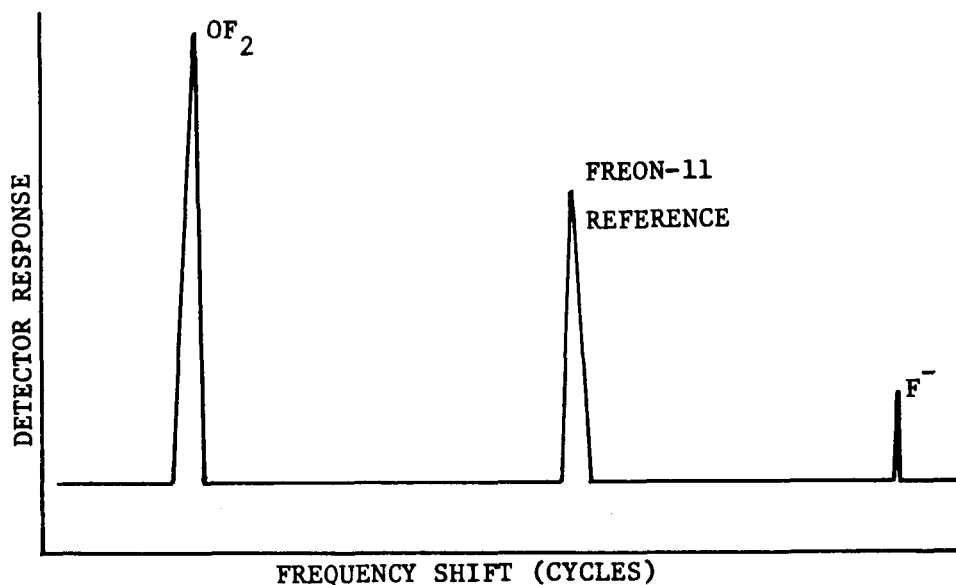
Surface of aluminum, titanium, stainless steel and most other metals are well coated with an oxide film 20 to 25 Å thick by virtue of the fact that we live in an oxidizing atmosphere. The oxide film is a form of dielectric which can be used to establish film thickness and film integrity. When the metal and its oxide film are combined with a proper conductor, an electrical circuit can be formed which will enable one to measure the impedance of the surface film. The impedance can be divided into capacitance and dissipative terms which give information about the film thickness and the presence of pin holes in the film. With the proper experimental techniques it should be possible to follow the rate of change of the oxide film thickness with time while in a propellant environment. It is expected that the effect of a reducing type propellant (e.g., N_2H_4) on the oxide layer would be quite different from that of an oxidizing type propellant (e.g., N_2O_4 or OF_2).

The sensitivity of the technique for this application has not been established nor has its practical utility been demonstrated. This technique has the potential, however, of being a valuable tool in generating qualification data in a short time.

5.3 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectroscopy is used to detect and distinguish between the nuclear particles present in a sample. The basic concept of the method is that an alternating magnetic field can induce transitions between the spin levels of the nucleus placed in a fixed magnetic field. These spin level transitions are detected by a radio receiver. In these respects NMR spectroscopy differs from conventional spectroscopy, which analyzes light and other radiation emitted or absorbed by the electron system surrounding the nucleus. The method is completely nondestructive.

An application of NMR spectroscopy to compatibility testing may be found in the determination of the stability of passivating fluoride films on materials in contact with oxygen difluoride or liquid fluorine. If the passivating film is attacked by the propellant and subsequently loosens and flakes off, it could be detected by the appearance of a specific NMR spectrum in the oxygen difluoride. The type of fluoride resonance spectrum that would be expected for such a situation is shown below:



There is no contribution from compounds of any element other than the one under study (e.g. F^{19}). Also note that the resonance response of OF_2 and fluoride ion are far removed and can be easily identified. The relative concentrations of different fluorine-containing compounds can be determined by measuring the areas under the respective peaks.

Conceivably, the NMR method could also be used to identify and measure hydrogen within steel or titanium alloy lattices. The NMR spectrum obtained from molecules in a solid, however, is generally much lower in intensity than in liquids so such an application is not expected to be competitive with the palladium foil hydrogen analyzer.

A comparison of these new techniques with existing methods is shown below in terms of sensitivity, flexibility, analysis time, and analysis cost.

Table 5-1 COMPARISON OF SENSITIVE TECHNIQUES

Technique	Sensitivity parts per million	Flexibility no.elements	Analysis Time, no. per hr (estimated)	Cost,* \$ per analysis (estimated)
Atomic Absorption	.0001 to 5.	67	4	5
Neutron Activation	1×10^{-7} to 10.	75	1	25
Palladium Foil Hydrogen Anal.	.01 to 0.1	1	4	5
Volatile Metal Chelates	1×10^{-8}	40-50	3	7
Surface Impedance	not established	-	not est.	not est.
Nuclear Magnetic Resonance	0.1 (F ⁻)	-	4	5

* Does not include initial equipment costs.

The initial conclusion drawn from this comparison was that the volatile metal chelate technique is extremely sensitive, moderately flexible, and costs somewhat less than the neutron activation technique. However, it does not possess some of the unique desirable qualities of the neutron activation method such as the nondestructive tracing of the movement of specific elements by means of a detector placed external to the system under study. The technical demonstration of the volatile metal chelate technique was recommended.

6.0 EXPERIMENTAL DEMONSTRATIONS

Four techniques for measuring material-propellant compatibility were chosen for experimental demonstration. These were selected on the basis of their newness and sensitivity. The purpose of the experiments was to demonstrate the ability of the technique to determine accurate interaction data in a short period of time and to show how that data can be correlated with interaction over the long term.

6.1 RADIOACTIVE TRACER TECHNIQUE

6.1.1 Theory

Certain atoms in the periodic table of elements contain nuclei which have an energy state that is considered in excess to the normal energy of that element. These species of the element are referred to as radioactive isotopes; they lose some of this excess energy periodically and statistically to produce nuclei of lower energy state and/or configuration. This loss of energy and reconfiguration is called radioactive decay or disintegration and is manifested in the emission of various particles and electromagnetic waves.

Radioactive elements are found occurring naturally or can be prepared artificially. Radioactive nuclei can be prepared through a variety of nuclear reactions, the most common being the capture of a low energy neutron by a stable nucleus. This is normally done in a nuclear reactor, although other neutron sources are available.

The radioactive decay of these elements begins immediately upon their formation and continues until no radioactive elements remain. The rate of change of the number radioactive elements in a particular set is proportional to the number present, N ,

$$dN/dt = -\lambda N \quad (1)$$

where λ is a proportionality constant known as the disintegration constant. The disintegration constant has been shown statistically to be independent of all known physical variables (e.g., temperature, pressure, electric and magnetic fields). If equation (1) is integrated, it can be shown that the disintegration constant is given by

$$\lambda = .693/t_{1/2} \quad (2)$$

where $t_{1/2}$ is the characteristic "half life" of the element i.e., the time required for one half of the quantity of radioactive element present to decay.

The use of radioactive elements as tracers depend on the ability to measure or observe the emissions given off by disintegrating nuclei. To do this, a suitably large disintegration rate must be attained and the measuring device must be responsive to whatever emissions occur.

In general, artificially produced radioactive isotopes are used as tracers. The rate of formation of radioactive atoms in a nuclear reactor is proportional to the number of atoms available for activation to the higher energy state, N_0 , the reactor neutron flux, ϕ , and the thermal-neutron (low energy) activation cross-section σ

$$dN/dt = N_0 \phi \sigma \quad (3)$$

At the same time that radioactive atoms are formed, some of those that were activated are decaying so that the net rate of formation is

$$dN/dt = N_0 \phi \sigma - \lambda N \quad (4)$$

The number of radioactive atoms present after time t can be found by solving the differential equation (4).

$$N = \frac{N_0}{\lambda} \phi \sigma (1 - e^{-\lambda t}) \quad (5)$$

It is worthy of note that when t is large ($t > t_{1/2}$), equation (5) reduces to

$$N\lambda = N_0 \phi \sigma \quad (6)$$

such that the rate of decay equals the rate formation and the radioactivity level attained is called the saturation activity. It is also significant that the level is directly proportional to that neutron flux, making that parameter important in choosing the source of neutrons used.

When t is small compared to $t_{1/2}$, the term $e^{-\lambda t}$ approaches $1 - \lambda t$ so that equation (5) reduces to

$$N = N_0 \phi \sigma t \quad (7)$$

Again the radioactivity level is proportional to the neutron flux so that for any given activation time the higher flux will produce the higher radioactivity level in the sample.

As a result of the two foregoing relations the following general comments may be made: nuclei with short half lives produce tracers with very high sensitivity; tracers with long half lives are not as sensitive but are more convenient to use.

The two relations above allow one to calculate the disintegration rate (known as the activity) of the radioisotope at the end of activation period t by using equation (1).

Radiation detectors are used to measure or observe the emissions given off by decaying radioisotopes. There is a variety of radiation detectors available covering the various types of emission known.

Type	Emission Detected
Scintillation detector	γ
Charged-particle Detector	β^+ , β^-
Semiconductor Detector	β^+ , β^- , α , γ

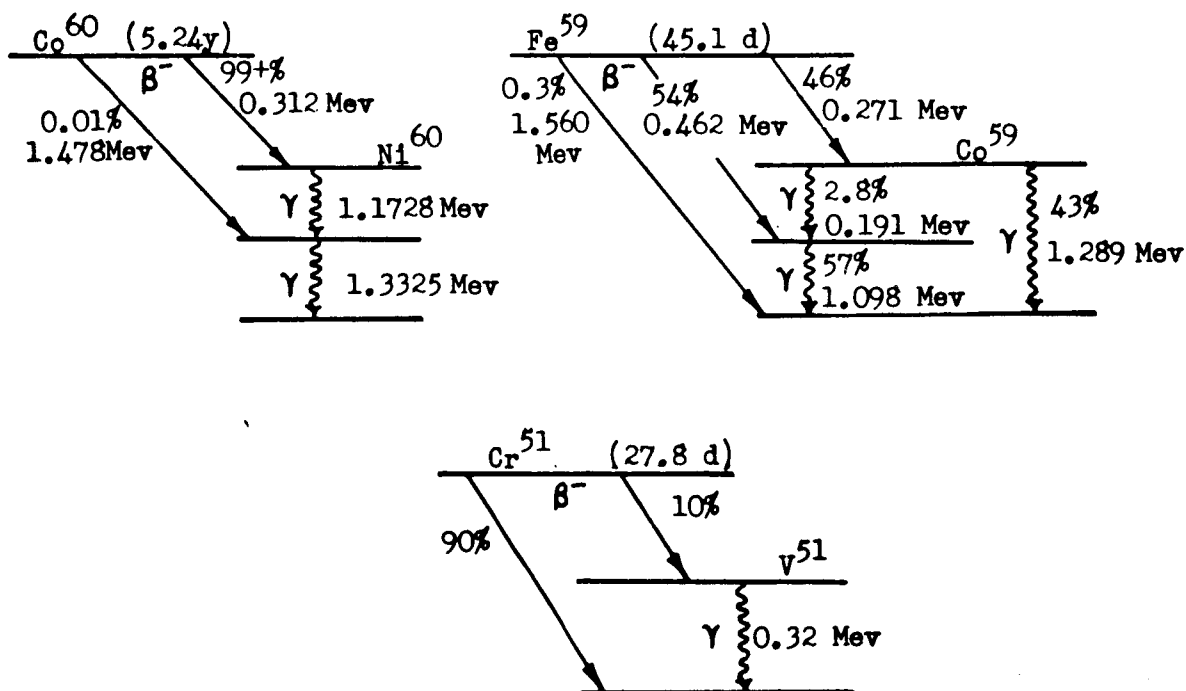
Since we are mainly concerned with gamma photon emission in this study, we will restrict discussion to the scintillation detector. The scintillation process involves the interaction of a gamma photon with a crystal of sodium iodide activated with thallium, NaI (Tl), to produce light. The light output from a NaI (Tl) detector is essentially a linear function of the photon energy over a wide energy range. A high gain photomultiplier is used to convert light impulses to electrical impulses. The combination of a NaI crystal and photomultiplier tube is called a "detector," whereas an assembly of detector, associated electronics, and readout devices is called a "counter". If the counter is capable of performing differential energy measurements, it is termed a "spectrometer."

In order to tell if the counter will be able to provide meaningful data, consideration must be given to the relation of the sample activity to the natural cosmic radiation background. In general, the count rate from the sample should be at least equal to that of the natural background. Statistical analysis shows that the count rate required is a function of the desired error limits and confidence level,

$$\text{error} = \pm n \sqrt{C}$$

where n is the number of standard deviations that corresponds to the desired confidence level and C is the total number of counts. The value of n is 1.645 for a confidence level of 90 percent.

It turns out that all disintegrations of radioisotopes do not result in a "count." If the detector is a type designed for gamma rays, no count will result from beta particles. Likewise, the emissions are statistically radiated into three-dimensional space, whereas the detector only intercepts a small fraction of these radiations. The type of radiation emitted depends on the radioisotope. Many radioisotopes emit several kinds of radiation and the distribution of each kind is unique to each isotope. For example, consider the decay scheme for several radioisotopes of interest:



Essentially all Co^{60} nuclei decay by way of the 0.312 Mev negatron transition, followed immediately by two gamma photons in cascade. The 45.1-day Fe^{59} nuclei decays by three negatron branches with the .271 Mev and .462 Mev transitions predominating. Immediate gamma emissions follow. For Cr^{51} , only 10% of the disintegrations result in gamma emissions. In addition, the detector equipment is somewhat less than 100% efficient. Because of geometrical considerations and the high penetrability of gamma rays, a large number of gammas are never observed by the detector. As a result the number of gamma emissions recorded by the detector as "counts" are considerable lower than the actual number of disintegrations which has occurred.

The relation for the attenuation of gamma rays penetrating a medium is

$$\frac{I}{I_0} = e^{-\mu x} \quad (9)$$

where I_0 is the original intensity and I is the intensity after passing a distance x through the medium. The absorption coefficient, μ , is a function of the medium and the energy level of the gammas. In general, the absorption increases with decreasing gamma energy. Thus the NaI detector crystal will absorb more (and thus have a greater response to) .32 Mev Cr^{51} gammas than it will 1.3 Mev Fe^{59} gammas.

The preceding considerations explain the experimental fact that the detector efficiency is about 15% at an energy of 1 Mev.

6.1.2 Experimental Considerations

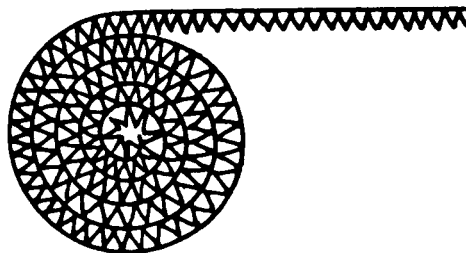
This section describes the materials and apparatus used in the experimental demonstration of the radioactive tracer technique. The experiment was designed to show how the radioactive tracer technique can be applied to the problem of detection of the interaction between a liquid propellant and a metallic material.

Propellant - The liquid propellant used in this demonstration was MIL-P-26536C hydrazine obtained from the Olin Mathieson Company. Routine assay of hydrazine by the chloramine-T method and trace analysis by atomic absorption were performed. Water content was determined by gas chromatography. Results of the analyses are recorded in Table 6-1.

Metal-Foil- The material chosen to demonstrate the interaction between hydrazine and a material surface was 0.5-mil Type 304 stainless steel foil. The foil was irradiated in the reactor at Washington State University at a neutron flux of 8×10^{12} neutrons/cm²/sec for a period of ten hours. The composition of the foil and the radioisotopes present after irradiation are shown in Table 6-2.

It is evident that there is a large number of elements present in stainless steel that can be successfully activated. In practice, however, it turns out that only a few of the elements in stainless steel are applicable to the present study. For a variety of reasons (low neutron cross-section, low natural abundance, very long half-lives, and no gamma emissions) the majority of the elements listed are not suited for detection by this method. In addition, the very short half-life isotopes have essentially decayed away before the foil is utilized in the experiment. The elements observed in the gamma spectrum of the stainless steel foil throughout the experiment were Fe⁵⁹, Cr⁵¹, Mn⁵⁴ and Co⁶⁰.

Apparatus - The experiment was carried out in a glass tube apparatus which is shown schematically in Figure 6-1. The foil was attached to a Teflon-covered magnetic stirring bar by a thin strip of unactivated foil cut from the same roll of 304 stainless steel. The activated foils had various configurations depending on the total surface area required. The smallest required surface area was a simple rectangle, approximately 0.5" x 1.0". The larger foil surfaces required that the foil be coiled up in an orderly fashion so that all of the foil was immersed in the hydrazine. To insure that the total available surface area was well wetted by the hydrazine, some means of separating adjacent layers of the coil was necessary. The method used was to alternate a strip of corrugated foil with one that was uncorrugated. The sketch below will serve to illustrate this concept.



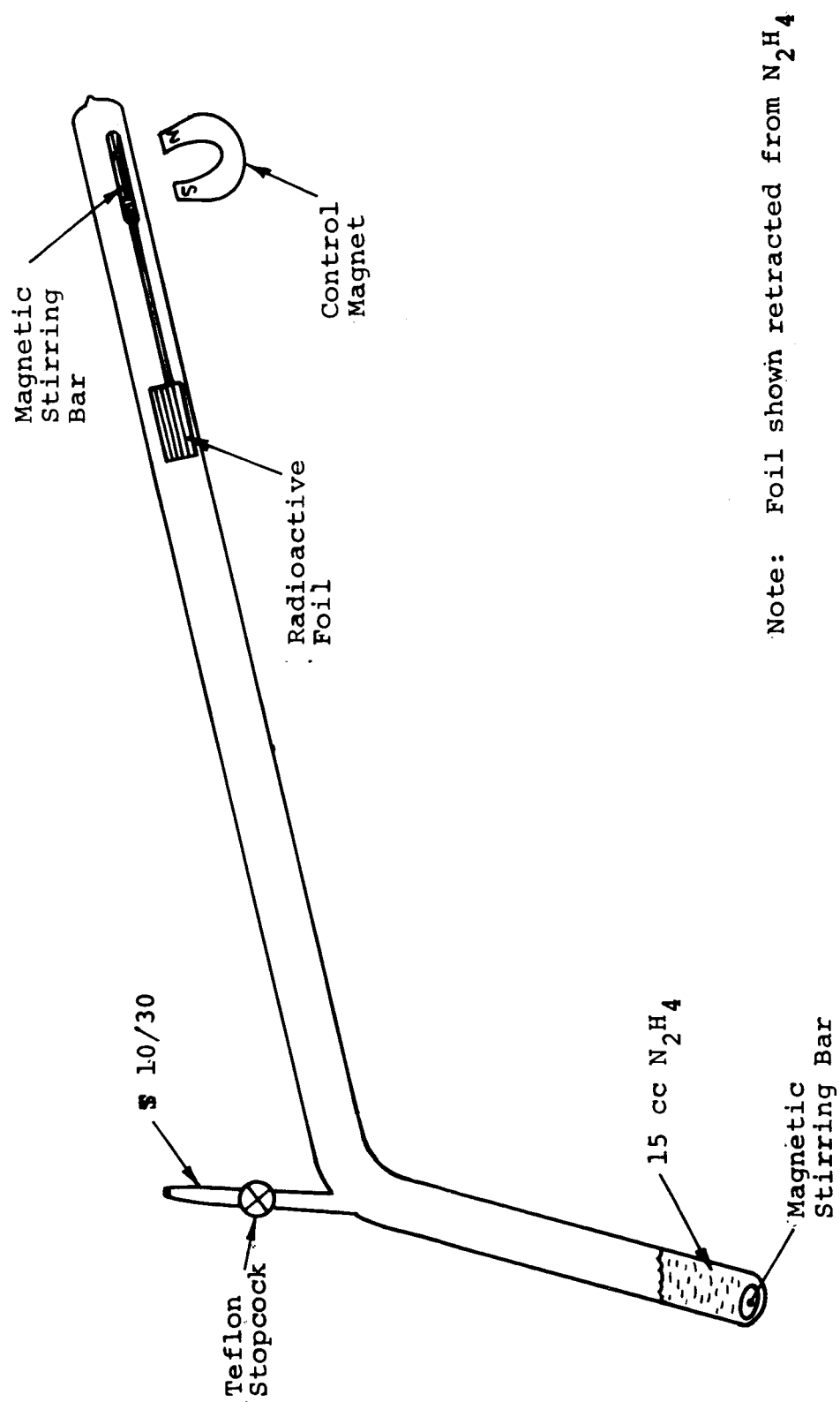


Figure 6-1: Reaction Apparatus for Hydrazine - Stainless Steel

Table 6-1 ASSAY OF MIL-P-26536C HYDRAZINE

Constituent	Spec Limits	Found
N ₂ H ₄ , %	97.5 min	98.3
H ₂ O, %	2.5 max	0.065
particulate, µg/ml	10 max	0.2
Fe, ppm	not required	0.2
Zn, ppm	not required	0.1
Cr, ppm	not required	0.2
Cu, ppm	not required	0.1

Table 6-2 STAINLESS STEEL CONSTITUENTS

	Nom. Spec, %	Found, % [†]	Active Species	Half Life
Iron	64.8	66.02	Fe ⁵⁹	45d
Chromium	20.0	19.46	Cr ⁵¹	27.8d
Nickel	12.0	9.54	Ni ⁶⁵ , Ni ⁶³	2.56h, 85y
Manganese	2.0	1.61	Mn ⁵⁶ , Mn ^{54*}	2.59h, 310d
Copper	-	.095	Cu ⁶⁴ , Cu ⁶⁶	12.8h, 5.18m
Molybdenum	-	.11	Mo ⁹³ , Mo ⁹⁹ Mo ¹⁰¹	6.75h, 67h, 14.6m
Cobalt	-	.07	Co ⁶⁰	5.25y
Silicon	1.0	not det'n	Si ³¹	2.6h
Phosphorous	.05	not det'n	P ³²	14.3d
Sulfur	.032	not det'n	S ³⁵ , S ³⁷	87.1d, 5.0m
Carbon	.1	not det'n	C ¹⁴	5700y

*From Fe⁵⁴,

†

By Atomic Absorption Spectroscopy

The strips used to form the coils were nominally one-inch wide. The surface area of the coils was determined by comparing the coil weight to the weight of an accurately measured piece of foil.

The gamma spectrometer used for counting consisted of a Harshaw Company 3" x 3" sodium iodide scintillation detector with a 1" x 1.5" well coupled to a photomultiplier tube whose output was amplified by a Boeing-designed charge sensitive preamplifier. The Boeing preamplifier fed a Technical Measurements computer and Model CN1024 multi-channel analyzer with tabular printout.

Procedure - All glassware was cleaned with dichromate cleaning solution at 60°F for 10 minutes then rinsed with deionized water until free of all acid. The glass tubes were then dried with a stream of dry nitrogen.

The metal foils were degreased with reagent grade acetone. Some early trial runs used foils which were not passivated. Subsequently, passivation was accomplished by treating the foils with 50-50 water-concentrated HNO_3 mixture for two hours, rinsing with deionized water to a neutral pH, and then drying under vacuum.

Hydrazine was added to the L-tubes by means of a clean 15-ml pipet. The hydrazine was then frozen with liquid nitrogen and the air pumped from the tube. An atmosphere of dry nitrogen was admitted and then the foil-magnet assembly was installed in the upper part of the tube and the end of the tube was sealed off.

Before the experiment was started, i.e., before the foil was lowered into the hydrazine, the L-tube assembly was mounted in the gamma counter apparatus and a background count was taken as a reference point (subsequently termed the tube background). Although well shielded, this tube background was significantly higher than the normal cosmic background because of the proximity of the radioactive foil to the detector. Its value was of the order of 85 to 35 counts-per-minute (cpm) compared to natural background of 60 to 25 cpm in the range from 0.3 Mev to 1.3 Mev.

The foil was lowered into the hydrazine for a period of time and then removed for the counting operation. On the larger foils (S/V ratios of 56 and 100), the coils were shaken sharply to remove as much liquid

hydrazine as possible. The coil was then positioned in the upper part of the tube and the tube was placed in the gamma counting apparatus.

6.1.3 Results

Examination of the gamma spectra for all tests conducted under this study indicated that at least four elements appear to dissolve in the hydrazine. The species that were identifiable were iron, chromium, manganese, and cobalt. Nickel was not observed, most likely due to its very short half-life (2.56h). The manganese that was found was Mn^{54} which originated from Fe^{54} via a fast neutron reaction. Manganese from the stainless steel as Mn^{56} was not observed because it also has a short half-life (2.59h).

In becoming familiar with the hydrazine-stainless steel system, several tests of short duration were run. The first of such tests was with distilled hydrazine. A foil surface area-to-liquid volume ratio (S/V) of 100 inch^{-1} was used. After 10 minutes of contact with stainless steel, the hydrazine showed a chromium content of 0.7 parts-per-million (ppm) and an iron content of 4.4 ppm. The magnetic stirring bar showed accumulation of bubbles of gas during this time, therefore the test was discontinued. This was the only investigation with distilled N_2H_4 . The remainder of tests were done with MIL-P-26536C hydrazine.

Among the preliminary tests were one-day exposures with $S/V = 100$ and mil spec hydrazine, both stirred and unstirred. The chromium concentration versus time for the stirred test is shown in Figure 6-2. The iron concentration was not detectable for the shorter immersion times without long counting times, which were not practical. It was determined during the unstirred test that it was impossible to simulate completely quiescent conditions. The very fact that the foil had to be removed from the hydrazine to effect a gamma count precluded any attempt to maintain quiescent conditions, especially for a short term test. For a much smaller foil surface-to-volume ratio and longer exposure times one would be more likely to approach quiescence. The above tests were with foil which had been degreased only. The remainder of the tests described below used stainless steel foil which had been passivated according to the procedure noted above, and all were stirred with Teflon-covered magnetic stirring bars.

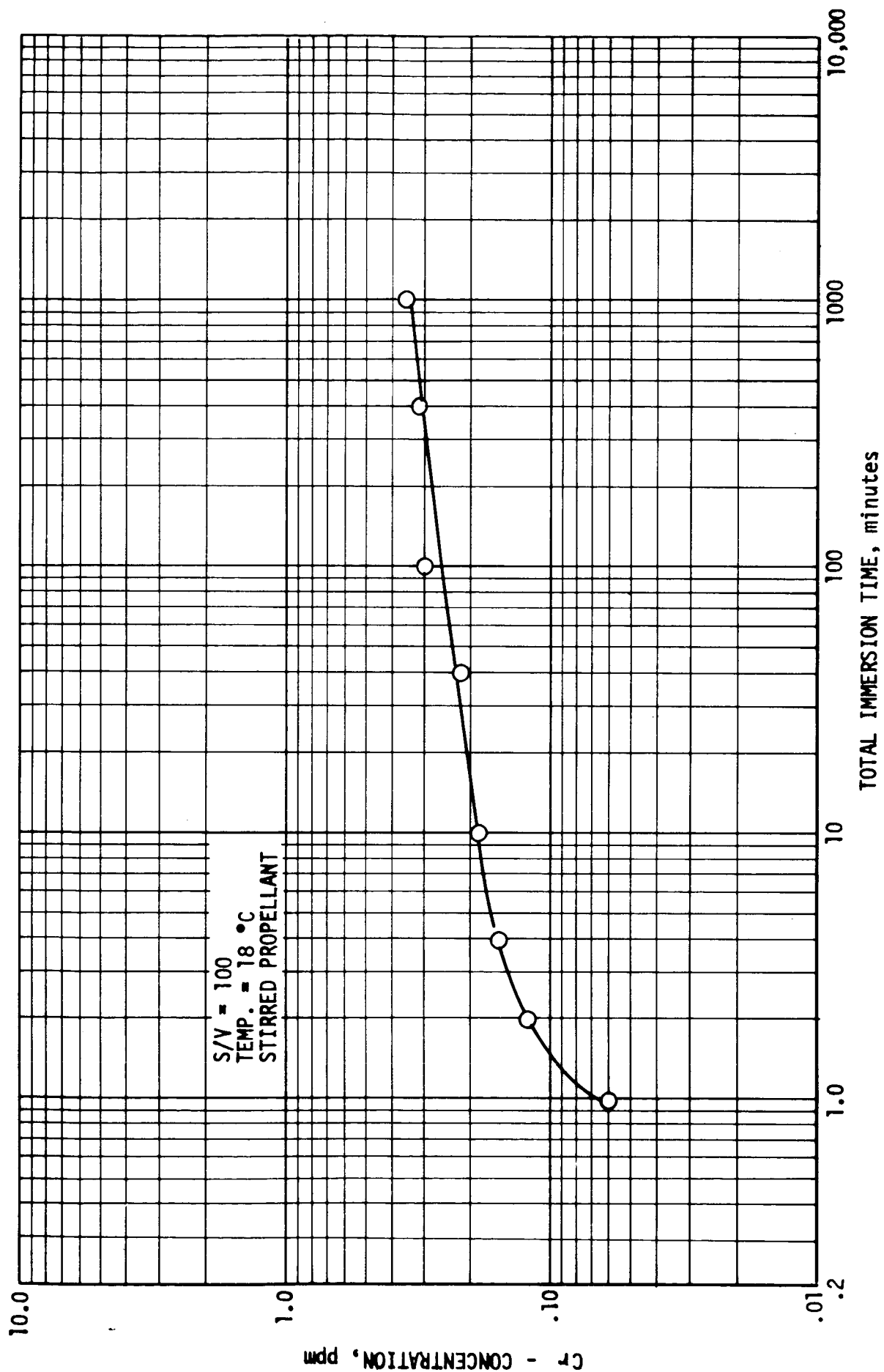


Figure 6-2:Cr Concentration for M11. Spec. $N_2H_4/304$ SS Foil Dissolution

Three experiments were run concurrently using passivated stainless steel foil of various surface areas and the same amount of hydrazine. The surface-to-volume ratios were 56, 11, and 1 inch⁻¹. Very little reaction was noted until 10,000 minutes (about 7 days) contact time had accumulated. After that time a steady increase in the concentration of iron and chromium was noted. The results are shown in Figures 6-3, 6-4, and 6-5. Whether or not the concentrations would continue to increase with time is a moot point. The tail-off at 200 days could be attributed to data scatter, but it is fairly consistent and atomic absorption analysis conducted at the completion of the experiment agrees well with the 200 day data. The low results for the atomic absorption method could be attributed to the occurrence of minute particles of foil which could separate from the major foil. These inhomogeneities would not be detected by the atomic absorption method but would have easily been detected by the gamma counter. The lower values from AAS could also be attributed to systematic error involved in the sampling of the hydrazine solutions for the AAS analysis.

The fact that no reaction was noted at the beginning of the experiment may be entirely due to the detection limit for iron and chromium. At the lower immersion times required at the beginning of the test, gamma counting times must be kept short so that small amounts of hydrazine adhering on the foil surface will not perturb the system giving erroneous dissolution data. When the immersion time becomes long compared to the counting time, the counting time can be increased, thereby improving the detection sensitivity.

The last three experiments were begun about 3-1/2 months after the foil was activated in the reactor. This corresponds to roughly two half-lives for iron and three and one-half half-lives for chromium. This itself lowered the detection sensitivity by one quarter and one tenth respectively. Thus the detection sensitivity could be increased in two ways; beginning the experiment sooner after activation and/or counting for a longer time where possible.

The interpretation of the information presented in Figures 6-3, 6-4, and 6-5 was the subject of some concern. The intent behind using various surface areas with the hydrazine was to enable one to correlate the short

DISSOLUTION OF STAINLESS STEEL BY HYDRAZINE

AT 25° C

Analysis by Radioactive Tracer

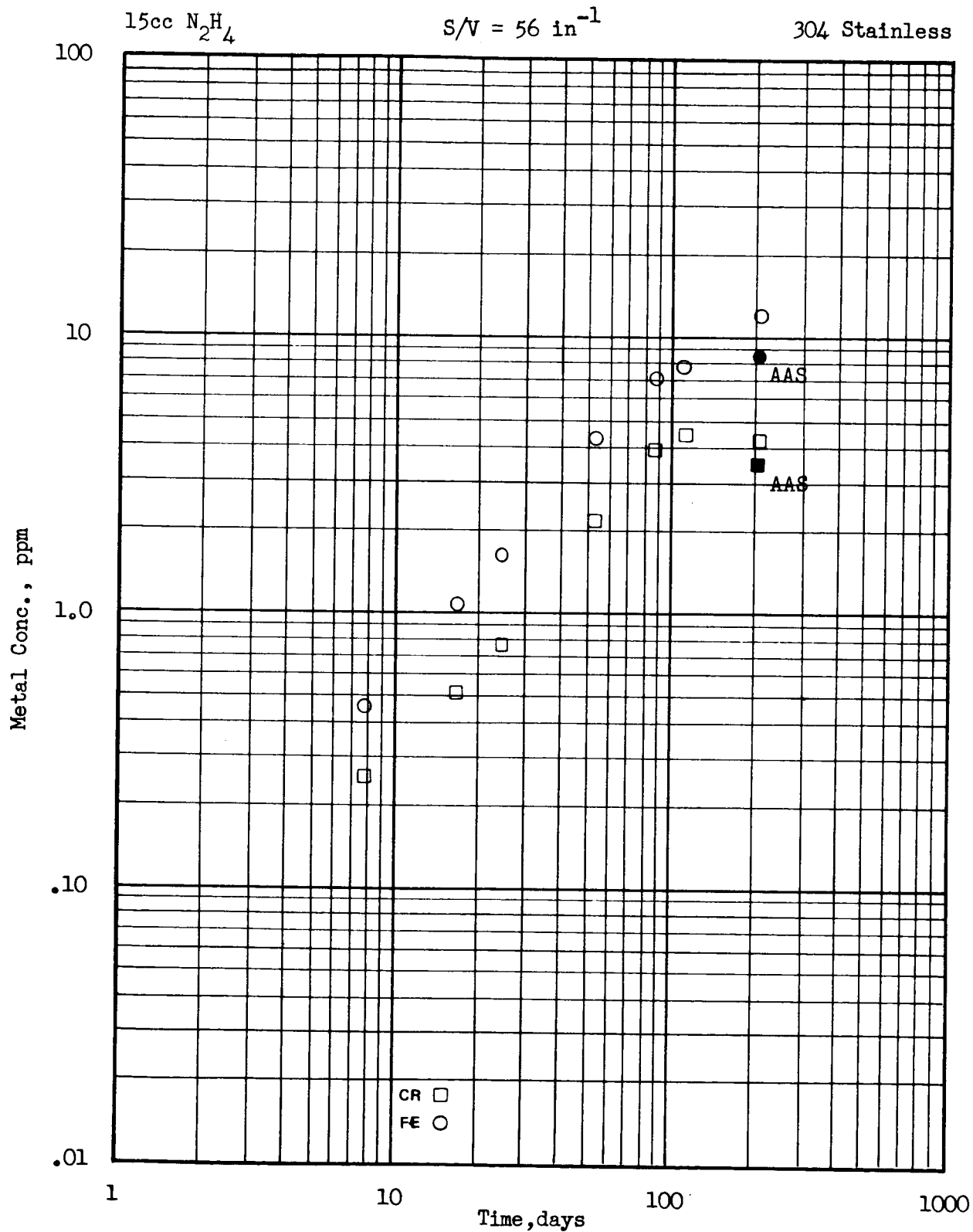


Figure 6-3: Metal Concentrations in Hydrazine vs. Time, $S/V = 56$

DISSOLUTION OF STAINLESS STEEL BY HYDRAZINE

AT 25° C

Analysis by Radioactive Tracer

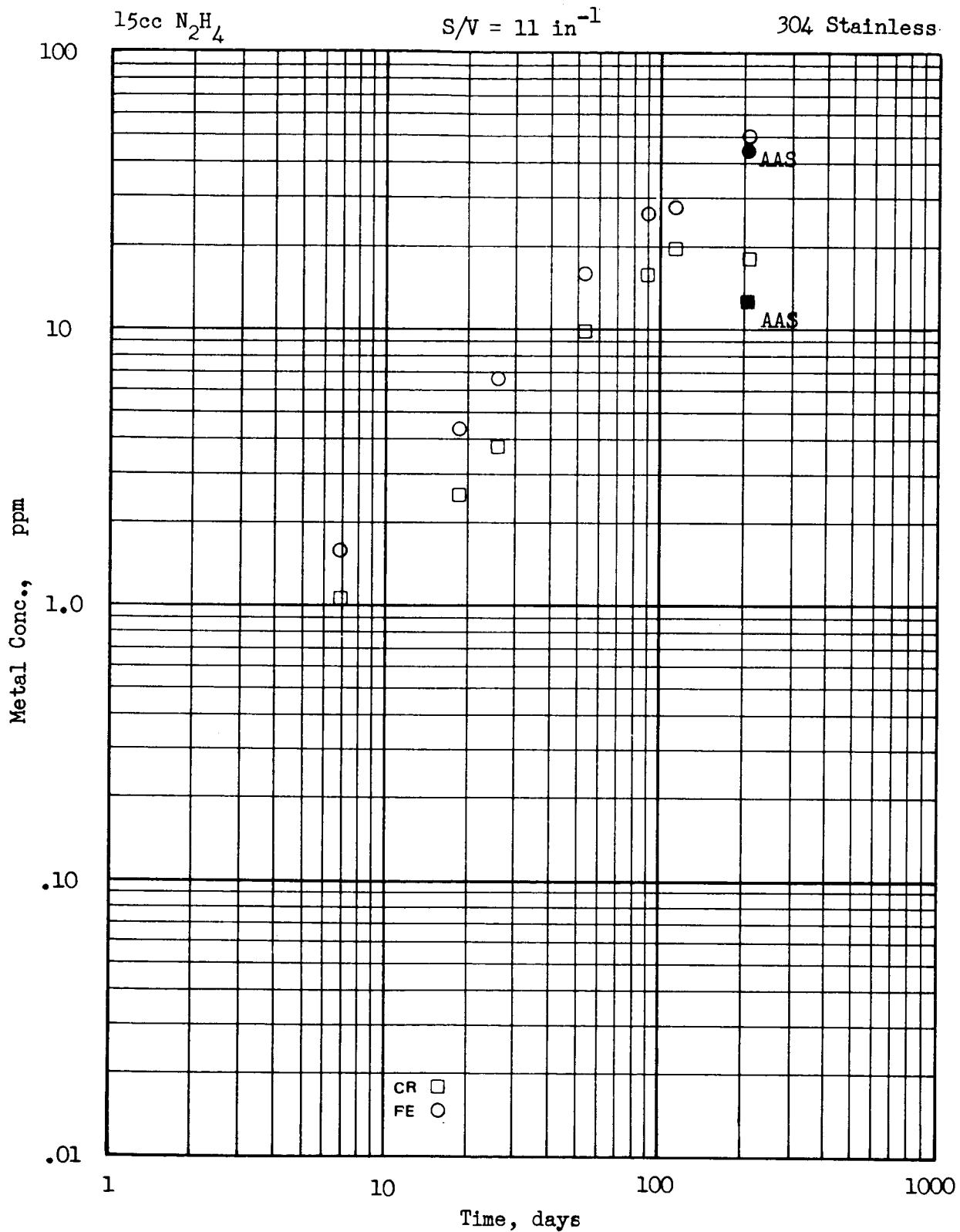


Figure 6-4: Metal Concentrations in Hydrazine vs. Time, $S/V = 11$

DISSOLUTION OF STAINLESS STEEL BY HYDRAZINE

AT 25° C

Analysis by Radioactive Tracer

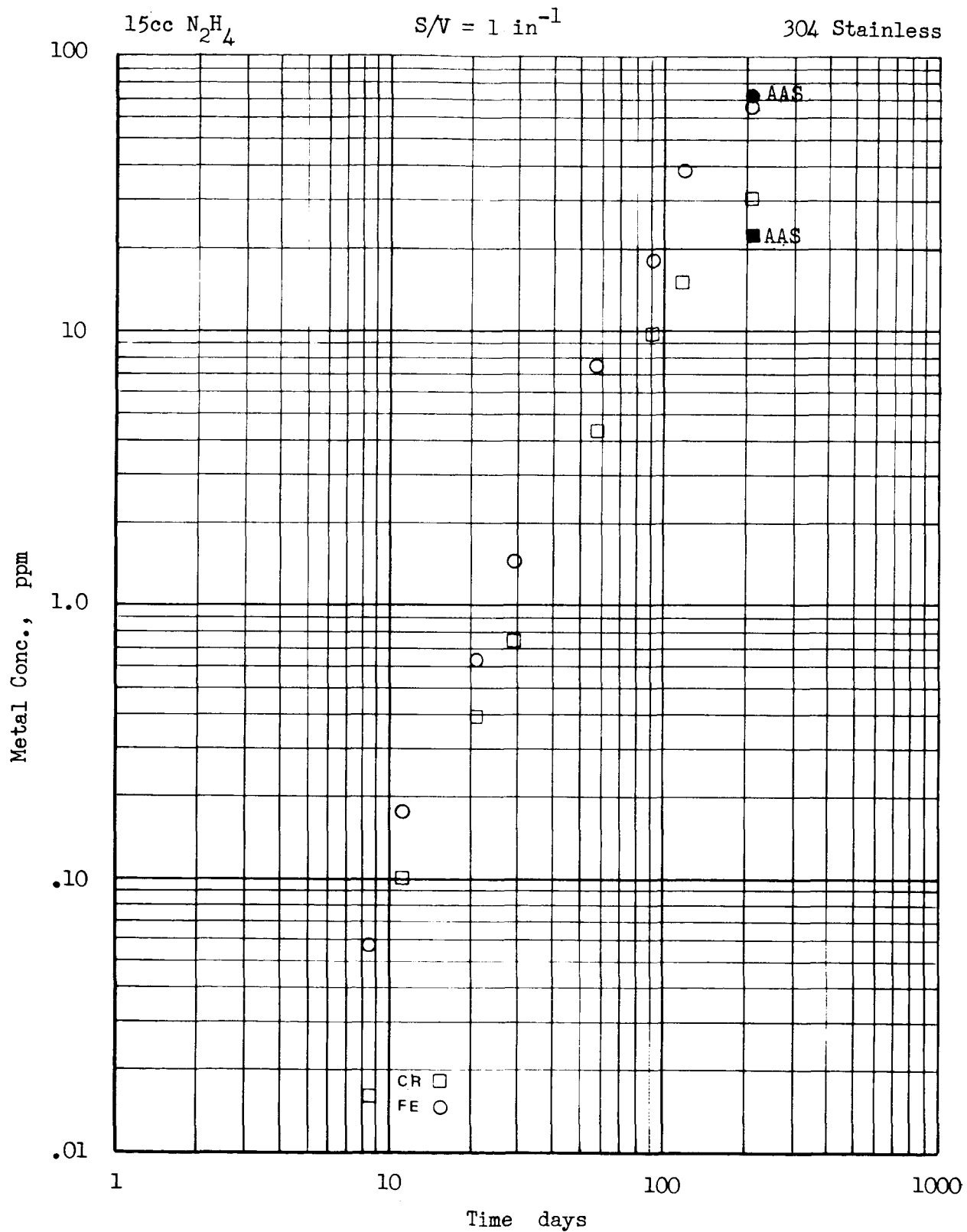


Figure 6-5: Metal Concentrations in Hydrazine vs. Time, $S/V = 1$

term data with expected interaction for the long term. The reasoning was that the rate of reaction of the hydrazine with the metal surface would be dependent on the surface area. Thus the surface reaction kinetics could be ascertained, allowing accurate extrapolation of data for any desired S/V ratios to any point in the future (at the temperature employed in this study). What in fact happened was that all three cases had essentially the same amount and rate of build-up of metal compound. Therefore the original assumption of a surface dependent reaction was not substantiated. A reasonable hypothesis for what happened was that the rate controlling substance was not surface of the foil but more likely was in the hydrazine. Such rate controlling substances may be water or carbon dioxide. This controlling factor may overwhelm the surface dependence and may well explain the crossing of the data for $S/V = 1$ over the $S/V = 56$ and 11 . Whether such substances are catalytic in nature or are exhausted in time could have a significant effect on the long term data and should be investigated. Such an occurrence could account for the tail-off at 200 days.

6.2 DRY ACTIVATION TECHNIQUE

6.2.1 Theory

The term "dry activation" refers to the process of activating a dry residue of material with thermal neutrons in a nuclear reactor to produce radioactive elements. The general theory for neutron activation technique was given in the section for the radioactive tracer technique. Some examples of the detection limits available for various metals of interest were given in Section 4.2 in Table 4-3. The theory will now be used to calculate the detection limit for aluminum.

Assume a 120 second activation in a neutron flux of $1.5 \times 10^{13} \text{ n/cm}^2/\text{sec}$ and a detector efficiency of 0.1% for a counting time of 300 seconds. This detector efficiency approximates that available with the germanium detector used at Washington State University (WSU). The observed background radiation was 0.12 counts per second in the aluminum gamma energy region. To insure a 90% confidence of a $\pm 10\%$ error in the sample counting, the sample counts must be at least 100 counts over 300 seconds which corresponds to .33 counts per second.

With a detector efficiency of 0.1%, a disintegration rate of 333 disintegrations per second is required. Using Equation 1 and

Equation 5 we find that the number of aluminum atoms required is given by

$$N_o = \frac{dN/dt}{-\lambda t (1-e^{-\lambda t})} \quad (10)$$

Using the information given, the value of N_o obtained is $2.3 \times 10^{14} \text{ Al}^{27}$ atoms and this corresponds to 1.2×10^{-8} grams. For a 10 gram sample of OF_2 , this amount of aluminum is equal to 0.001 ppm. This is a very practical detection limit for aluminum. With a sodium iodide well detector, the detector efficiency would be of the order of 10% and the detection limit would lower to .00006 ppm.

6.2.2 Experimental Considerations

Propellant - The propellant used in this study was oxygen difluoride manufactured by Allied Chemical Company. Chemical analysis of the OF_2 gas phase was performed by infrared spectral analysis (Beckman IR-12) and by mass spectrometry (DuPont 21-110B). The IR spectrum showed about 1-2% CF_4 and a trace of SiF_4 . The mass spectrum showed, in addition, trace amounts of HF , CO_2 , N_2 and O_2 . The purity of the Allied OF_2 was estimated to be in excess of 95%. The OF_2 was handled in stainless steel and glass vacuum lines. The gas was passed through a hydrogen fluoride scrubber (a tube packed with NaF) and used without further purification.

Metal Foil - The material selected to be used in this demonstration test was 6061-F MilQQA aluminum alloy. The alloy was obtained in the form of 2.5-mil foil from Crawford Foil Company, Hawthorne, California. No analysis of the metal foil was performed.

Apparatus - The container material for the exposure of liquid oxygen difluoride and 6061 aluminum was selected with care. It was desirable to conduct the experiment in the container that was to be used in the activation of the dry residue so as to minimize handling and transfer operations. Therefore, a requirement for the container material was that it be compatible with liquid oxygen difluoride and with the thermal neutrons in the nuclear reactor. The material should not have elements present that when activated, give interfering gamma radiation. Glass was ruled out for this reason. A sample of the second choice, Teflon, was sent to WSU for a trial irradiation. Teflon is considered compatible

with OF_2 and it was felt that activation of the fluorine in Teflon to produce F^{20} would not be harmful because of its very short half-life (12 seconds). The trial activation, however, showed that a relatively long lived interference resulted, rendering Teflon useless for the purpose intended. The interfering element(s) was not identified and Teflon was eliminated from further consideration.

Polyethylene is widely used in neutron activation analysis because of its desirable properties and relative freedom from impurities. While the material is not generally considered to be compatible with oxygen difluoride, limited contact for short periods of time should be possible provided that sensible safety precautions and rigorous cleanliness are observed. Two-dram polyvials (Olympic Plastic Company, Los Angeles, purchased from Van Roger and Waters Company, catalog number 66017-026) were subjected to simple compatibility tests with room temperature OF_2 gas and liquid OF_2 at temperatures between -320°F and the OF_2 boiling point. No violent reaction was observed in either case. The extent of interaction was a yellowing of the polyethylene and a deterioration of the surface to a tacky state. The polyethylene was thus judged adequate for the limited time of service required by this experiment (about 6 hours), and was chosen for use in the OF_2 - aluminum interaction study.

The polyvial was placed in a 20-mm Kimax glass tube fitted with a 10/30 inner glass joint. Figure 6-6 shows the polyvial and the glass tube. After the polyvial was inserted into tube, the bottom of the tube was sealed and the polyvial was positioned at the bottom. The vial was held tightly in place by the tab of the cap (which had previously been cut off), thus minimizing any tendency of the vial to float when liquid OF_2 was condensed into the tube.

The Kimax tube was attached to a glass vacuum line which was, in turn, connected to the gas manifold source of OF_2 . 3M Kel-F number 90 halocarbon grease was used on all ground joints. Valves used with the glass vacuum line were of the Fischer-Porter 4mm Teflon-glass type.

The remainder of the apparatus used in conjunction with the activation analysis was located at the WSU Radiation Center, Pullman, Washington. It consisted of the nuclear reactor, pneumatic transfer



FIGURE 6-6: OF_2 - ALUMINUM REACTION APPARATUS

system and associated controls, a gamma spectrometer utilizing a germanium solid state detector, and a high speed printer. The gamma spectrometer by Nuclear Data is shown in Figure 6-7; the Hewlett-Packard high speed printer can be seen in the lower right hand corner.

The pneumatic transfer system is used for radiations of elements whose radioisotopes have short half-lives. This insures rapid handling of samples to obtain maximum sensitivity. The operation of the pneumatic transfer system is programmed and automatically controlled. The control console and sample input lock is shown in Figure 6-8. The pneumatic transfer system delivers the sample directly to the counting room in a polyethylene "rabbit." The rabbit and polyvial are shown in Figure 6-9.

Standards - The standards used for this study consisted of quantities of pure metal each embedded with a hot glass rod in the surface of the bottom of a separate 2-dram polyvial. The metals (which represent each known metallic element in 6061 aluminum), their masses, and their purities are given below.

Table 6-3 ACTIVATION AND ANALYSIS STANDARDS

Element	Mass, grams	Purity, % metal
Al	.000110	99.997
Cu	.000101	99.999
Cr	.000155	99.93
Fe	.000175	99.99
Mg	.000108	99.995
Mn	.000110	99.4
Ti	.000109	99.96
Zn	.000102	99.7

Procedure - All glassware and polyvials were cleaned with distilled water and were dried. The foil was cleaned according to the following procedure: Degrease with reagent acetone, immerse in 50/50 nitric acid/water for one hour at room temperature, rinse with distilled water to a neutral pH, and allow to dry in air. The cap of each polyvial was cut off leaving a small tab on the side. This provided a means of maintaining a tight fit of the polyvial in the 20 mm tubing. The square of aluminum

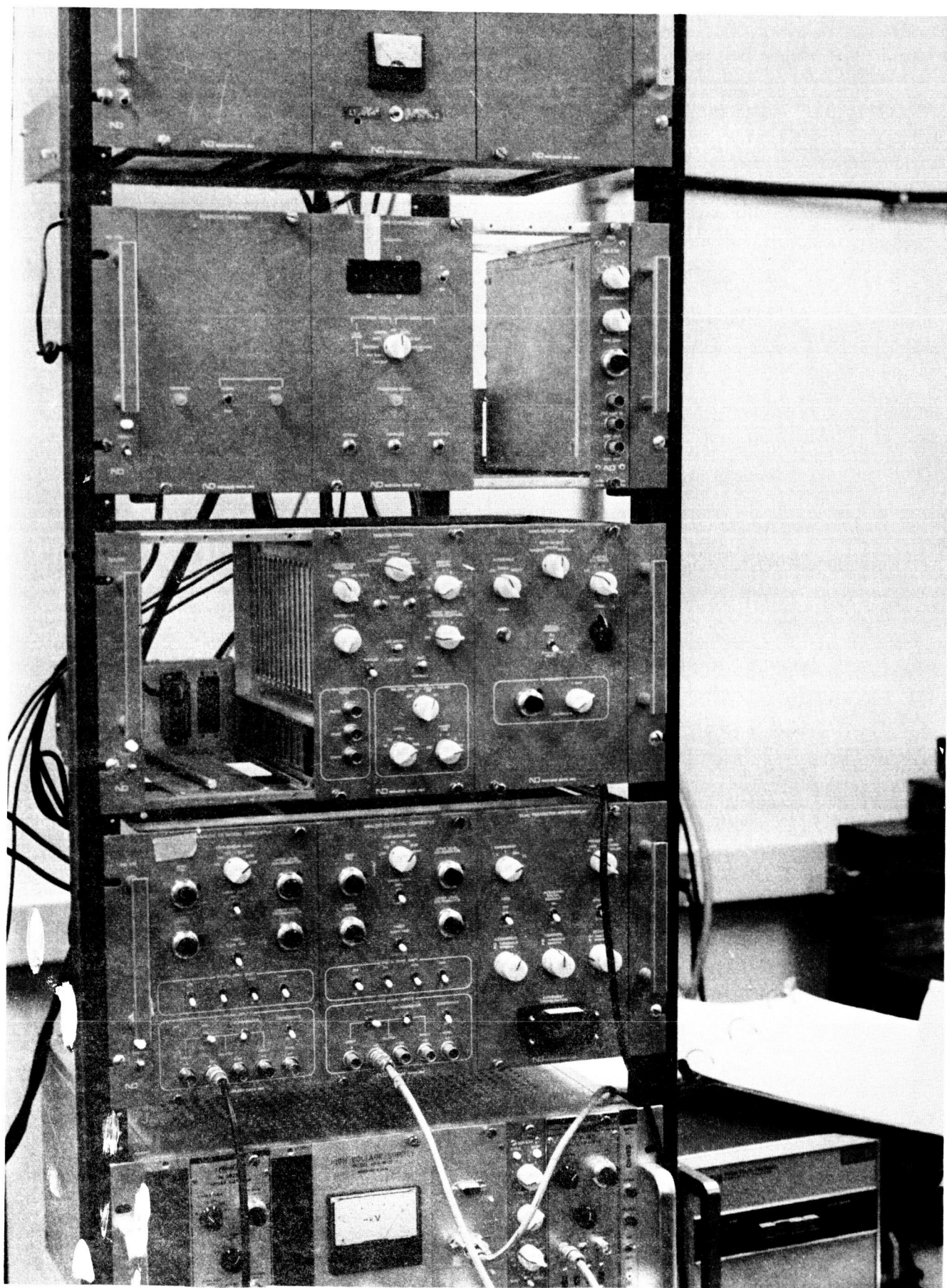


FIGURE 6-7: WSU GAMMA SPECTROMETER

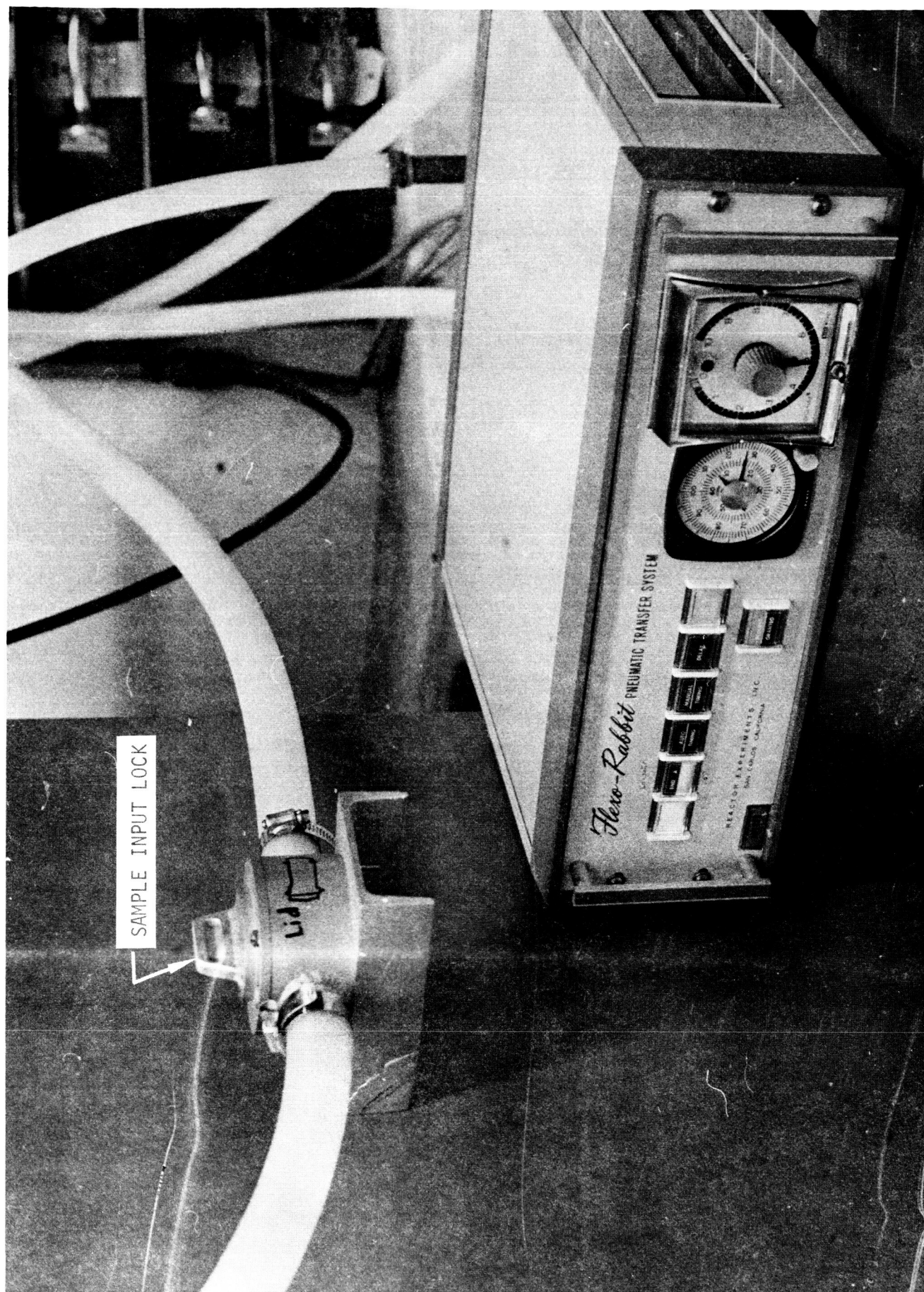


FIGURE 6-8: AUTOMATIC PNEUMATIC TRANSFER SYSTEM

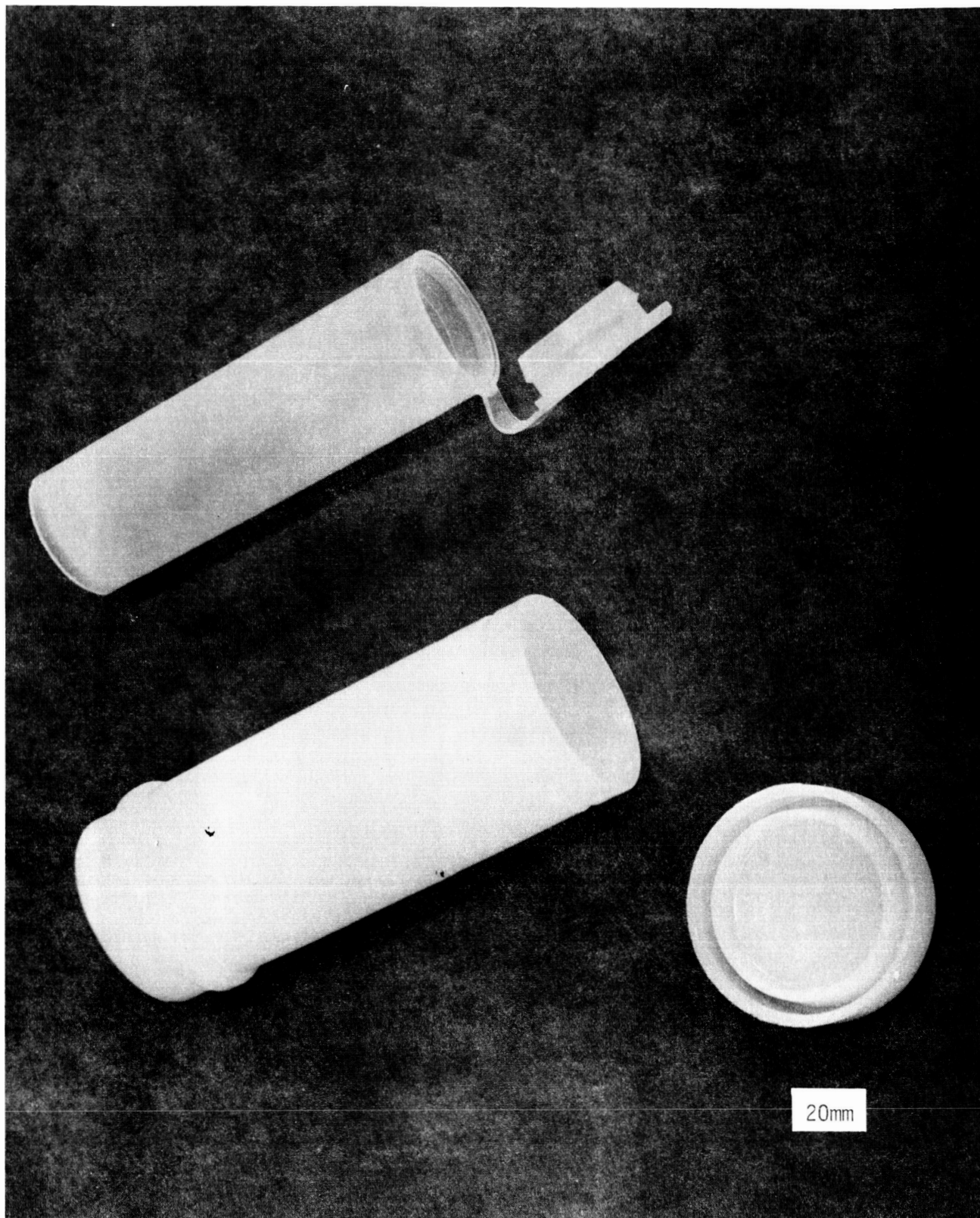


FIGURE 6-9: PNEUMATIC SYSTEM RABBIT AND POLYVIAL

foil was wedged in the polyvial in such a manner that the top of the foil indicated the liquid level required for 5.0 ml. A photograph of such an installation was shown in Figure 6-6. The polyvial was then positioned in the glass tube and the bottom sealed. The tube was attached to the glass vacuum line using Kel-F 90 grease as a sealant. Oxygen difluoride gas was introduced into the tube at room temperature to passivate the polyvial and foil surfaces. The OF_2 was then condensed in the bottom of the polyvial using a liquid nitrogen bath around the glass tube. As soon as the liquid level reached the top of the aluminum foil, the OF_2 was warmed to -248°F with a slush bath of dichlorodifluoromethane (Freon-12 or equivalent). The sample was held at this temperature for the required length of time after which the liquid was removed by evaporation into a liquid nitrogen cold trap.

The polyvials were subsequently removed from the glass tube and the cap replaced during transportation. Just prior to irradiation, the polyvial was flushed with nitrogen to remove atmospheric argon (which also activates) and the cap was heat sealed on with a hot glass rod. Each sample was irradiated for two minutes with the exception of the first two (blanks), which were irradiated for five minutes each. The five minute irradiations caused the polyvials to become excessively hot and melt inside of the rabbit, therefore, the irradiation time was reduced to two minutes. The samples were then counted with the gamma spectrometer for a period of 200 to 300 seconds each. Depending upon the radioactivity of the sample, the polyvial was placed on one of ten calibrated shelves above the detector face. In Figure 6-10, a sample is shown being counted on shelf 3. This arrangement allows a wide range of sample activities to be accommodated, yet preventing an overloading of the gamma spectrometer.

6.2.3 Results

The appearance of the aluminum foils after contacting liquid oxygen difluoride was, for the most part, unchanged. A photograph of the exposed and unexposed foils is shown in Figure 6-11. The bent corners were used for identification. On those samples exposed for the longer

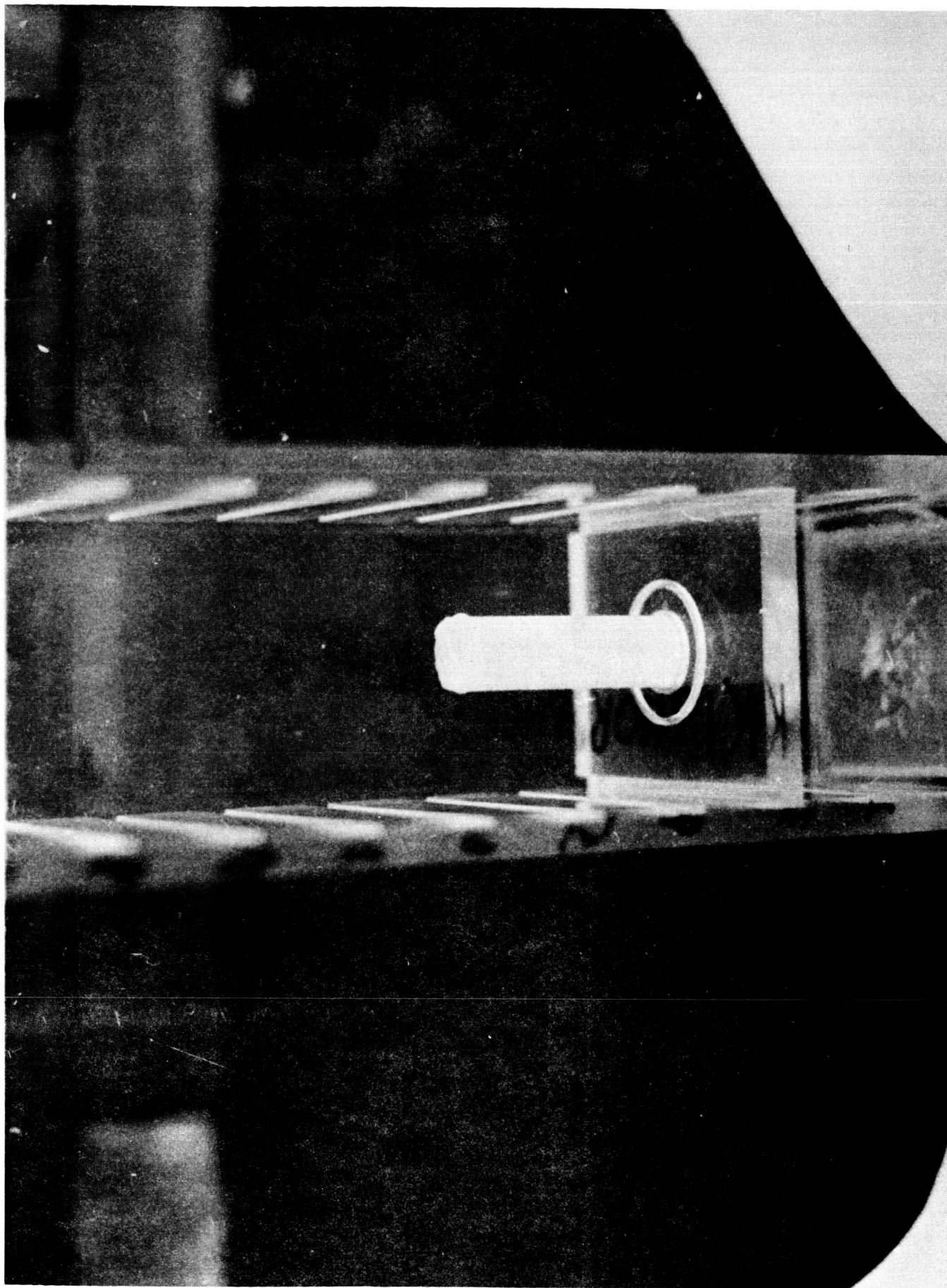


FIGURE 6-10: COUNTING OF IRRADIATED POLYVIAL

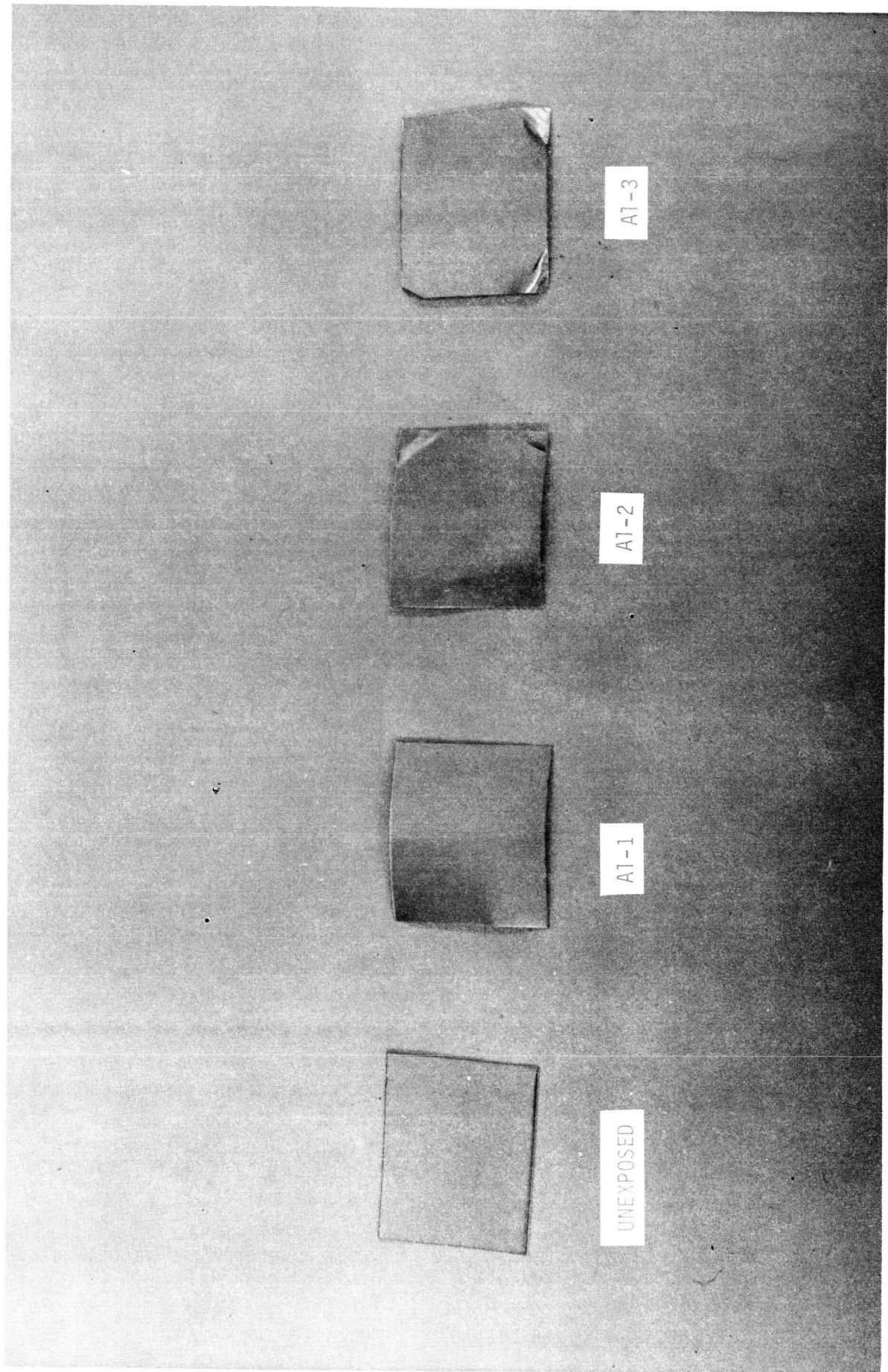


FIGURE 6-11: FOILS AFTER CONTACT WITH OF₂

periods of time, there appeared some small white spots reminiscent of "hard water" spots. No gross etching was noted. This is in agreement with the findings of TRW⁽⁵¹⁾. The results of the activation analysis on the residue in the polyvials indicated the presence of aluminum and a trace amount of manganese.

Examination of the gamma spectra of all standards and blanks indicated the presence of aluminum. The amount of aluminum in each case was random and averaged about 0.8 micrograms. It was concluded from this information that the aluminum samples would also have random amounts of aluminum contamination. The source of this aluminum contamination was identified to be the aluminum pneumatic transfer tubes in the reactor. While the polyethylene vials are encased in polyethylene rabbits during irradiation, continued handling of the rabbits (albeit carefully) inevitably causes transfer of aluminum (probably in the form of Al_2O_3) on the outside of the rabbit to the inside of the rabbit. Also, as the rabbits are propelled into the reactor in the pneumatic transfer system, they undoubtedly impact on the bottom of the aluminum tube in the reactor with substantial force causing an invisible cloud of aluminum oxide dust to billow up and surround the rabbit. This dust may well permeate the rabbit cap seal resulting in aluminum dust contaminating the polyvial inside. Another potential source of the aluminum was certain collection bags at the terminal of the pneumatic transfer system. The terminal of the pneumatic transfer system is shown in Figure 6-12; a clear plastic bag is taped to the delivery tube at the bottom of the picture just out of view. As each rabbit is delivered at the terminal, a small quantity of radioactive dust is dumped into the bag along with the rabbit. Consequently the bag was replaced with a fresh one after every six or seven deliveries. The collection bag was located only a few feet from the gamma detector, thus, some contribution due to aluminum oxide in the bag could be expected in the gamma spectra. No correlation could be established between sample queue position, the number of times the bag had been used, and the aluminum background. Furthermore, a second activation and count of the aluminum samples and a blank with no collection bag in proximity to the detector produced higher aluminum counts than the previous analysis. This points out that handling and contact with the rabbit are the major

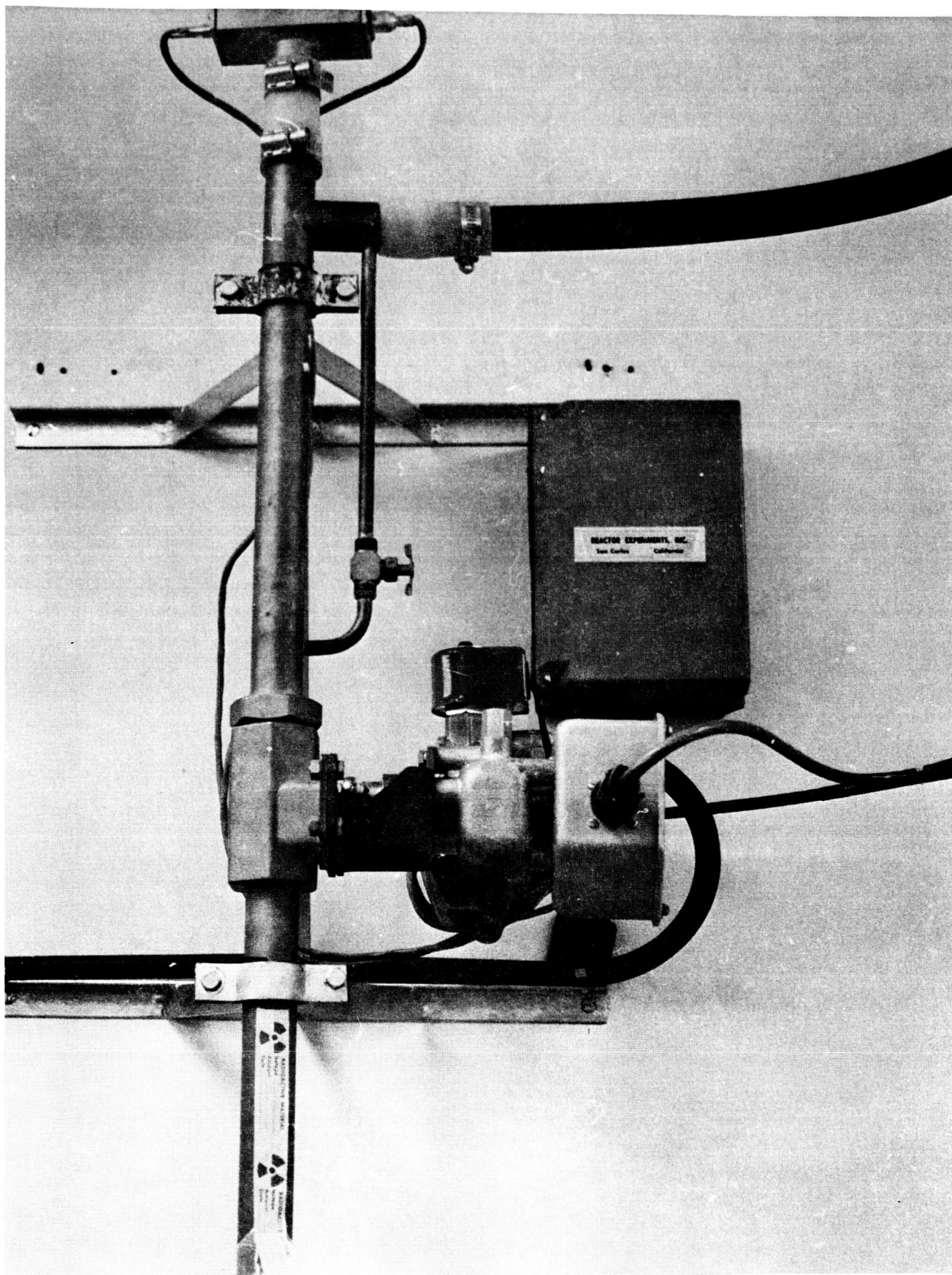


FIGURE 6-12: PNEUMATIC TRANSFER SYSTEM TERMINAL

sources of aluminum contamination. Elimination of this problem is straightforward: use of new unused rabbits for aluminum analysis coupled with careful handling of the polyvials before and after activation.

The random aluminum oxide background for the standards and blanks was averaged and subtracted from the aluminum found in the polyvials. The results of this test are summarized in Table 6-4. The uncorrected values for aluminum are also shown as an upper limit.

Table 6-4 INTERACTION OF OXYGEN DIFLUORIDE WITH 6061 ALUMINUM

5 ml OF ₂ @ -248°F			5.1 cm ² Surface Area		
Sample Identification	Temperature of Liquid, °F	Exposure Time, hr.	Foil Surface Appearance After Contact with OF ₂	Aluminum Found in OF ₂ , ppm	Upper Limit To Aluminum Found in OF ₂ , ppm
Al-1	-321	0.2	Unchanged	0.8	1.6
	-248	0.1			
Al-2	-321	0.5	Unchanged	0.3	1.2
	-248	0.6			
Al-3	-321	0.1	Slight appearance of white deposits	1.0	2.0
	-248	5.4			

6.3 PALLADIUM FOIL HYDROGEN MEASUREMENT

6.3.1 Theory

The phenomenon of the diffusion of hydrogen through palladium has been attributed to the solubility of hydrogen in the metal (Dushman and Lafferty ⁽⁵²⁾). Diffusion occurs by motion of the atoms (or protons in the case of hydrogen) along interstitial sites in the metal crystal lattice. It can be shown that the rate of diffusion of a diamotic gas through a metal to an evacuated side is

$$q = k_o (P_{mm})^{.5} \exp (-b_o/T) / d \quad (11)$$

where d is the metal thickness, P the pressure in mm of Hg and k_0 and b_0 are constants for a given gas-metal system. Notably, at constant pressure the rate of diffusion increases exponentially with the temperature. In a more convenient form and somewhat different units, the above can be expressed as

$$\log_{10} Q_{\mu l} = C - B/T \quad \frac{\text{micron} \cdot \text{liters}}{\text{cm}^2 \cdot \text{mm} \cdot \text{min}} \quad (12)$$

For hydrogen-palladium, $C = 4.5765$ and $B = 2296$ (Barrer, 1940) (53). The fact that hydrogen diffuses through palladium much more readily than through any other metal is utilized for the introduction of the pure gas into an evacuated system.

In the palladium foil hydrogen analyzer (PFHA), the occurrence of hydrogen diffusing through the palladium is detected by a cold-cathode ion pump. The ion pump is normally used in ultra-high vacuum systems where a low pumping speed is adequate. According to Dushman and Lafferty:

The cold-cathode ion pump is basically a variation of a Penning-type ionization gauge consisting of a ring anode and two cathode plates in a magnetic field . . . The anode is operated at high positive potential with respect to the cathode. Electrons emitted by the cold cathode are forced into a spiral path by the presence of a strong magnetic field. The increased electron path results in a high probability for collision and ionization between electrons and gas molecules. The positive ions then bombard the cathode and sputter metal from the cathode. The sputtered metal deposits in various regions of the tube, forming stable compounds with the chemically active gas molecules.

During operation, the cathode current is monitored and the process of positive ion bombardment manifests itself as an increase in cathode current. Thus, the amount of gas being pumped is proportional to the ion pump cathode current.

6.3.2 Experimental Considerations

Propellant - The propellant used for this demonstration was diborane which was purchased from the Callery Chemical Company, Callery,

Pennsylvania. An analysis of the diborane purity was performed by infrared (IR) and mass spectrometric (MS) analysis of a sample taken directly from the refrigerated shipping container.

The IR analysis was performed in the gas phase using a Perkin-Elmer Model 112 spectrometer. The spectrum was compared with a spectrum of diborane which had been distilled four times. The spectra were identical.^(54,55)

The mass spectrum was obtained using a Varian MAT CHS mass spectrometer. The spectrum mass numbers were identified and the background was subtracted. The resulting mass spectrum was that typical of pure diborane⁽⁵⁵⁾. It was concluded that the diborane shipped in a dry-ice refrigerated cylinder showed no significant decomposition and that the diborane was pure to at least the detection limit (about 10 ppm).

Apparatus - Diborane was stored at -230°F over a period of three months in the materials of interest. Metal vessels of high pressure capacity were fabricated from 6Al-4V titanium, 6061-T6 aluminum, and Type 304 corrosion resistant steel. The vessels were fitted with stainless steel NUPRO H series bellows valves rated for usage to 1000 psi pressure with toxic, hazardous, and corrosive fluids. The aluminum and stainless steel vessels were fabricated from tube stock and 1-inch stainless steel AN fittings. The titanium vessels were machined from 1.5-inch 6Al-4V titanium bar stock and fitted with 1.5-inch stainless steel AN fittings. Figure 6-13 shows the three types of vessels, as assembled. During the experiments the liquid contacted only the metal of primary interest whereas the vapor was allowed to contact the stainless steel valves and fittings.

The arrangement used to transfer gases from the metal vessels to the PFHA apparatus was constructed of heat resistant glass. The overall configuration is shown in Figure 6-14.

The PFHA apparatus consists of an electrolysis cell, a tubular oven with a palladium foil barrier, and an evacuated portion attached to a Varian ion pump. It is also attached to the glass transfer apparatus and a helium gas source. The helium gas sweeps the sample through the electrolysis cell and past the heated palladium foil barrier. The gases

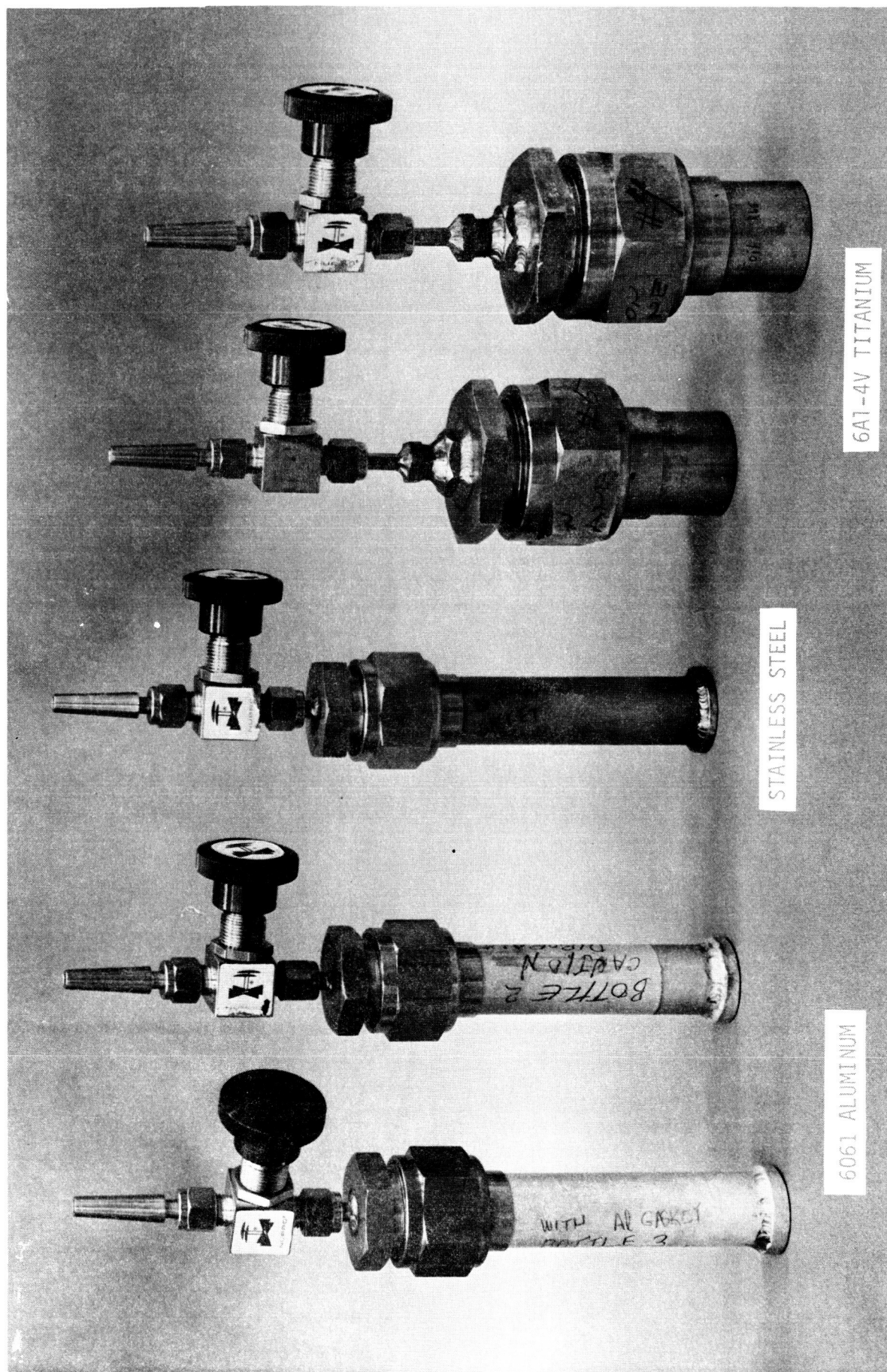


FIGURE 6-13: DIBORANE REACTION VESSELS

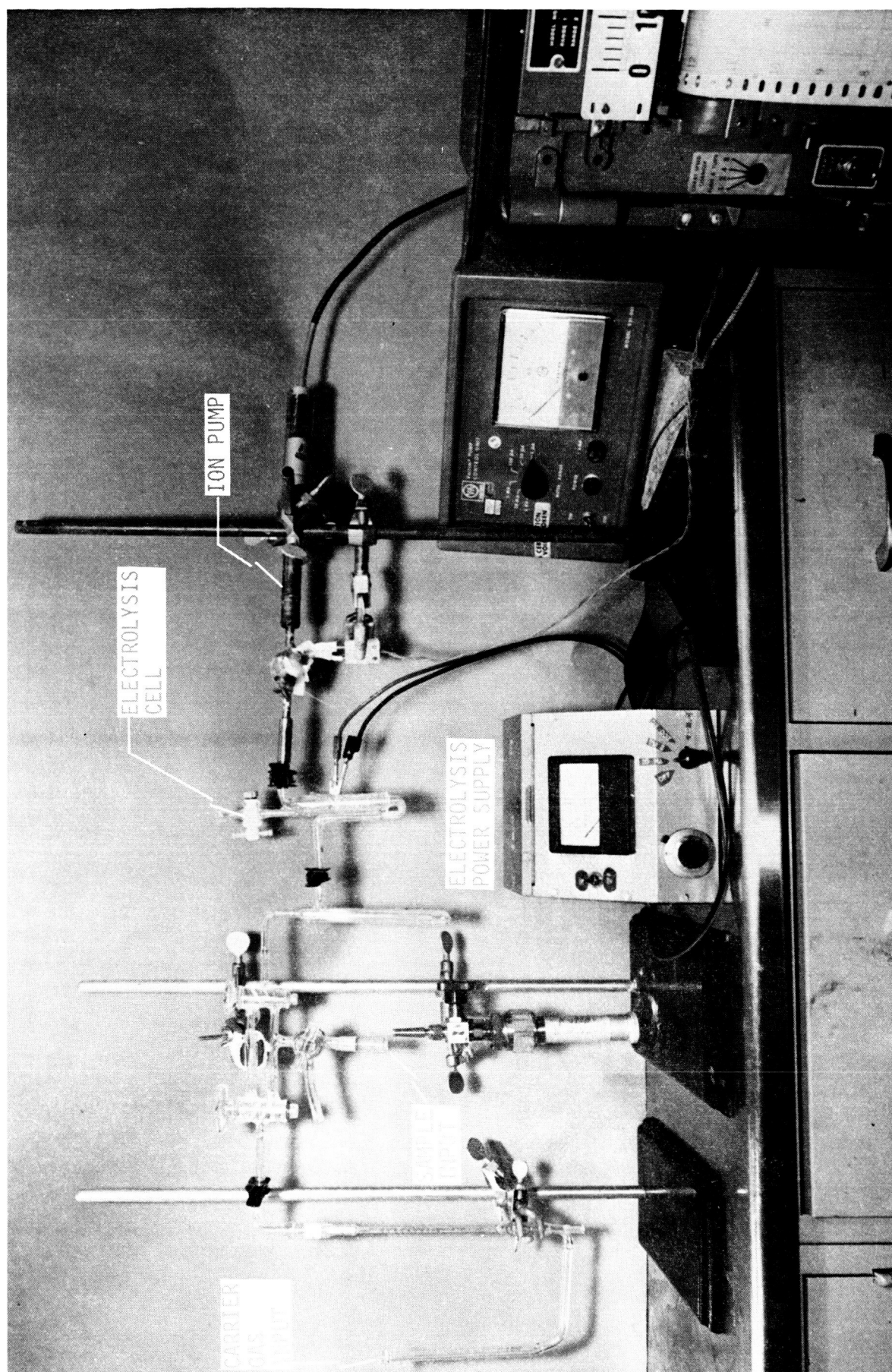


FIGURE 6-14: PALLADIUM FOIL HYDROGEN ANALYZER

then exit near the foil to the atmosphere. The amount of hydrogen that passes through the palladium is proportional to the partial pressure of hydrogen in the carrier gas stream.

Calibration - Calibration of the PFHA was accomplished by means of an electrolysis cell situated in the carrier gas stream. Small amounts of current through the electrolysis cell produced known amounts of hydrogen which were carried by the gas stream to the palladium foil. According to Faraday's law of Electrolysis one equivalent weight of hydrogen is produced for each 96,488 ampere seconds of electricity. The equivalent weight of hydrogen is 1.008 grams so that 1.05×10^{-5} grams of hydrogen are produced for each ampere second.

Currents on the order of 100 microamperes or less for one minute through the electrolysis cell produced measurable output at the ion pump which was continuously recorded on a strip chart. The areas under the peaks produced by the hydrogen generated at various current levels were used to prepare calibration curves relating peak area to quantity of hydrogen passed.

Procedure - All metal vessels were thoroughly cleaned and dried according to the following procedure:

- 1) Immerse in aqueous 45% HNO_3 at room temperature for one hour,
- 2) Rinse with distilled water until completely free of all acid (check with pH paper),
- 3) Bake at 140 to 160°F until dry.

Stanford Research Institute Report 951581-8⁽⁵⁶⁾ states that

... metallic surfaces in contact with diborane do not need to be passivated; however, it is stressed that all systems must be thoroughly cleaned to remove organic impurities and metal oxide scale.

Therefore, no treatment of the metal surfaces was used other than the cleaning procedure.

To the titanium and aluminum vessels (one each) were added metal foil of the same alloy to increase the surface area by a factor of ten. The foils were coiled up in a manner similar to that described on page 47.

The vessels were evacuated and helium leak tested to insure that there would be no diborane leakage out or air leakage into the vessels during the storage time of three months.

The diborane was distilled twice and twenty cubic centimeters (at -256°F) were transferred to each vessel. The vessels were then stored in a custom refrigerated container, cooled to -230°F by cold nitrogen gas as shown in Figure 6-15. This container was much more economical in its use of liquid nitrogen than a commercial environmental box. The vessels were monitored periodically for the formation of hydrogen using the PFHA.

To sample the gas over the diborane, the liquid diborane was frozen with liquid nitrogen to -320°F at which point diborane has negligible vapor pressure. The bottle was then attached to the PFHA sample inlet and the inlet area was evacuated. The gas from the metal vessel was then expanded into the inlet area and the vessel valve closed off. The carrier gas was then diverted through the inlet area, sweeping the gas sample to the palladium foil.

6.3.3 Results

The results of the analyses performed over the three month storage time are shown below.

Table 6-5 TOTAL HYDROGEN (IN GRAMS) FOUND OVER DIBORANE DURING STORAGE IN METALLIC CONTAINERS

<u>Vessel Type</u>		<u>Storage Time</u>		
		10 days	30 days	90 days
304	Stainless Steel	3.2×10^{-7}	-	-
6061	Aluminum	-	-	-
6061	Aluminum & Foil	1.6×10^{-6}	8.1×10^{-6}	1.4×10^{-5}
6Al-4V	Titanium	-	1.7×10^{-7}	1.1×10^{-7}
6Al-4V	Titanium & Foil	6.8×10^{-6}	6.3×10^{-6}	4.2×10^{-5}

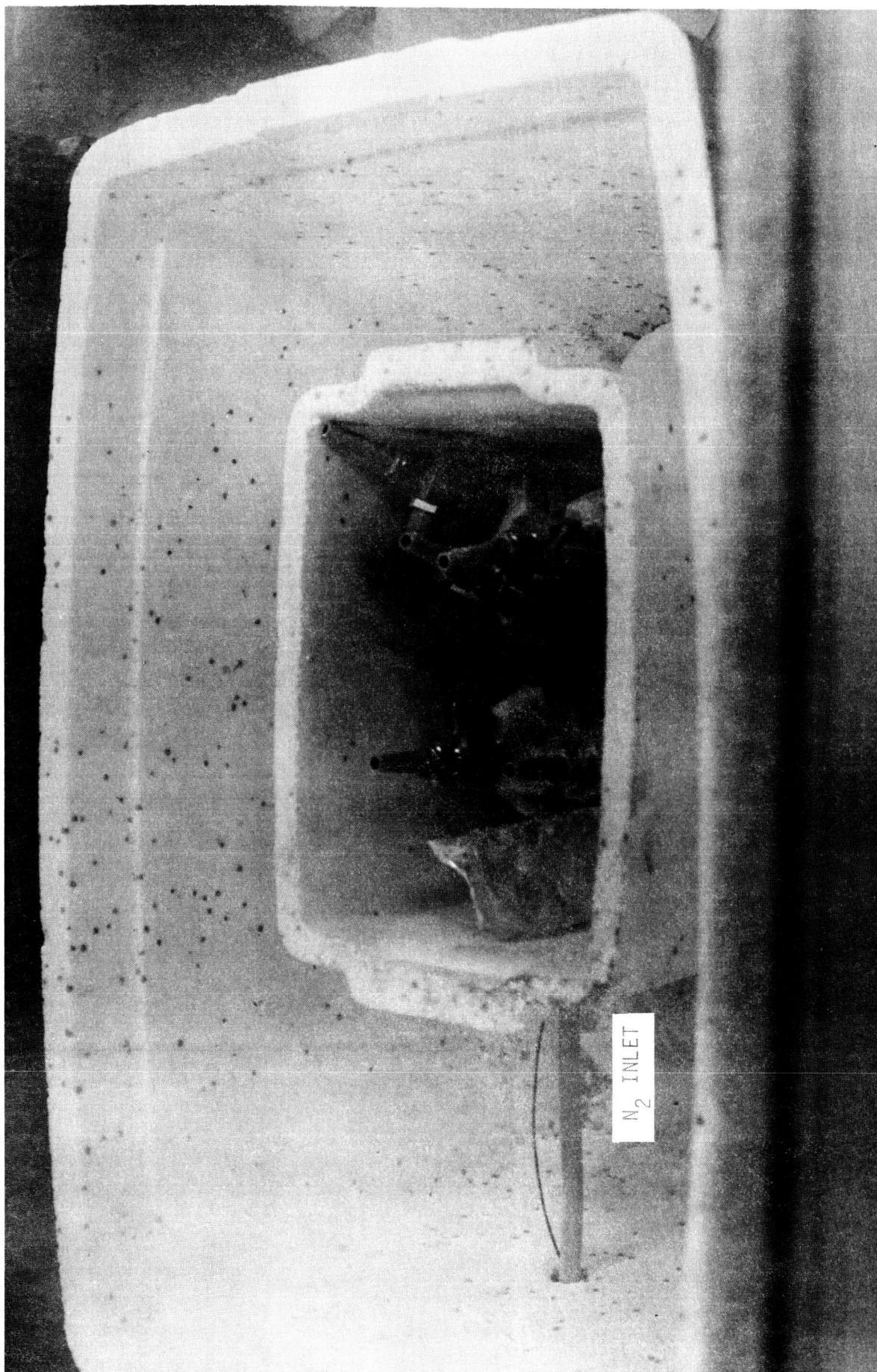


FIGURE 6-15: DIBORANE STORAGE REFRIGERATOR

These figures include corrections for expansion of the gases from the metal vessels into the sample area. The expansion was about 14% of the original gas volume. If all the hydrogen were dissolved in the diborane, the hydrogen could be reported as parts-per-million. Values of ppm would be approximately 10^5 times the value in the above table.

The wetted surface area for those vessels which contained foil was approximately ten times that with no foil in the vessel. If the buildup of hydrogen is directly proportional to the surface area (data suggests some dependence), the hydrogen observed for the vessels with foil added would be representative of that expected in the vessels after about two and one-half years at -230°F .

It is evident that interaction between diborane and stainless steel, aluminum, and titanium produces very little hydrogen gas over the liquid so that no difficulty would be expected from the standpoint of hydrogen buildup. On the other hand, certain metals have the capability to "accept" a certain amount of the steady state hydrogen concentration. Although these experiments showed negligible hydrogen evolved, they did not show how much hydrogen was taken up by the metal. The PFHA is also well suited for conducting such analyses quickly. It would be possible to show whether more or less hydrogen was taken up by the metal than was found as free gas. This may be important for the 6Al-4V titanium alloy which begins to show embrittlement when hydrogen levels reach approximately 125 ppm in the alloy.

6.4 VOLATILE METAL CHELATE ANALYSIS

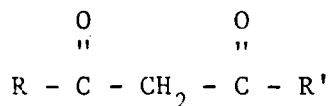
Under the task, Development of New Technology, a new technique for trace metal analysis was reported. This technique, using volatile metal chelates and a mass spectrometer, was given a preliminary experimental examination. Encouraging results prompted the addition of this technique to those to be demonstrated.

6.4.1 Theory

The use of the mass spectrometer is generally limited to gases or liquids that have a significant vapor pressure. Solids must be examined by special techniques such as vaporization by spark. Typically metals

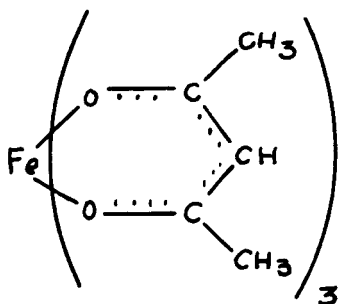
have presented difficulties for analysis by mass spectrometer, especially when seeking trace metals in a matrix of principal metal.

The present technique calls for the conversion of a metal to a metal chelate (Gk., claw) by use of a class of chemical compounds termed β -diketones. The β -diketone has the following general chemical structure



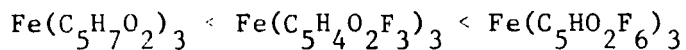
where R and R' are aliphatic hydrocarbon or fluorocarbon groups.

The reactions of this class of compound with metals have been well known for a long time. A typical reaction product with iron would be



which is commonly called acetylacetonate, iron (III). The compounds are stabilized through resonance within the unsaturated six-membered ring. Most of the compounds of this type are stable at relatively high temperatures and are somewhat volatile. These features also make them useful for work with gas phase chromatography.

The substitution of the methyl group hydrogens by fluorine in the ligand tends to increase the chelate's volatility. That is, listed in increasing order of volatility, we find,



Moshier and Sievers⁽⁵⁷⁾ explain the volatility of the fluorocarbon chelates:

The greater volatility of the fluorocarbon chelates appears to be a general phenomenon. The reason for this is not clear,

but several possible explanations have been advanced. The increase in volatility may be due to a reduction in van der Waals' forces and perhaps to a decrease in intermolecular hydrogen bonding in the fluorine-containing chelates. Molecular models of octahedral hexafluoroacetylacetonate chelates show that a large portion of the periphery is occupied by the eighteen highly electronegative fluorine atoms encasing the metal ion in a fluorocarbon shell. The resulting intermolecular attracting forces are weaker than in the unfluorinated complexes. Conceivably the somewhat bulkier fluorine atoms could prevent close-packing in the crystal lattice, a factor that should favor greater volatility.

The volatility of this class of compounds is such that quantitative analysis may be obtained rapidly using a mass spectrometer.

An added feature of the fluorinated β -diketones is that many of them react directly and quantitatively with metals and metal compounds to form metal chelates.

The mass spectrometer, as its name implies, produces a spectrum based on the masses of the species analyzed. Moreover, under the influence of the ionizing electron beam in the mass spectrometer source, molecular fragments of the parent specie are formed whose type and distribution are characteristic of the parent molecule.

The mass spectrometer used in this study was the DuPont 21-110B shown in Figure 6-16. This instrument utilizes the Mattauch ⁽⁵⁸⁾ type analyzer which combines the high resolving power of double focusing with the ability to record a fairly wide range of masses simultaneously. Briefly, the analyzer consists of tandem electrostatic and magnetic sectors as shown in Figure 6-17. A beam of ions of mixed mass and velocity emerges from the object slit and travels down the field drift tube into the electrostatic sector. After traversing the electrostatic sector, where velocity focusing occurs, the ion beam enters the magnetic sector where it is separated into a series of beams composed of the



FIGURE 6-16: DUPONT 21-110B MASS SPECTROMETER

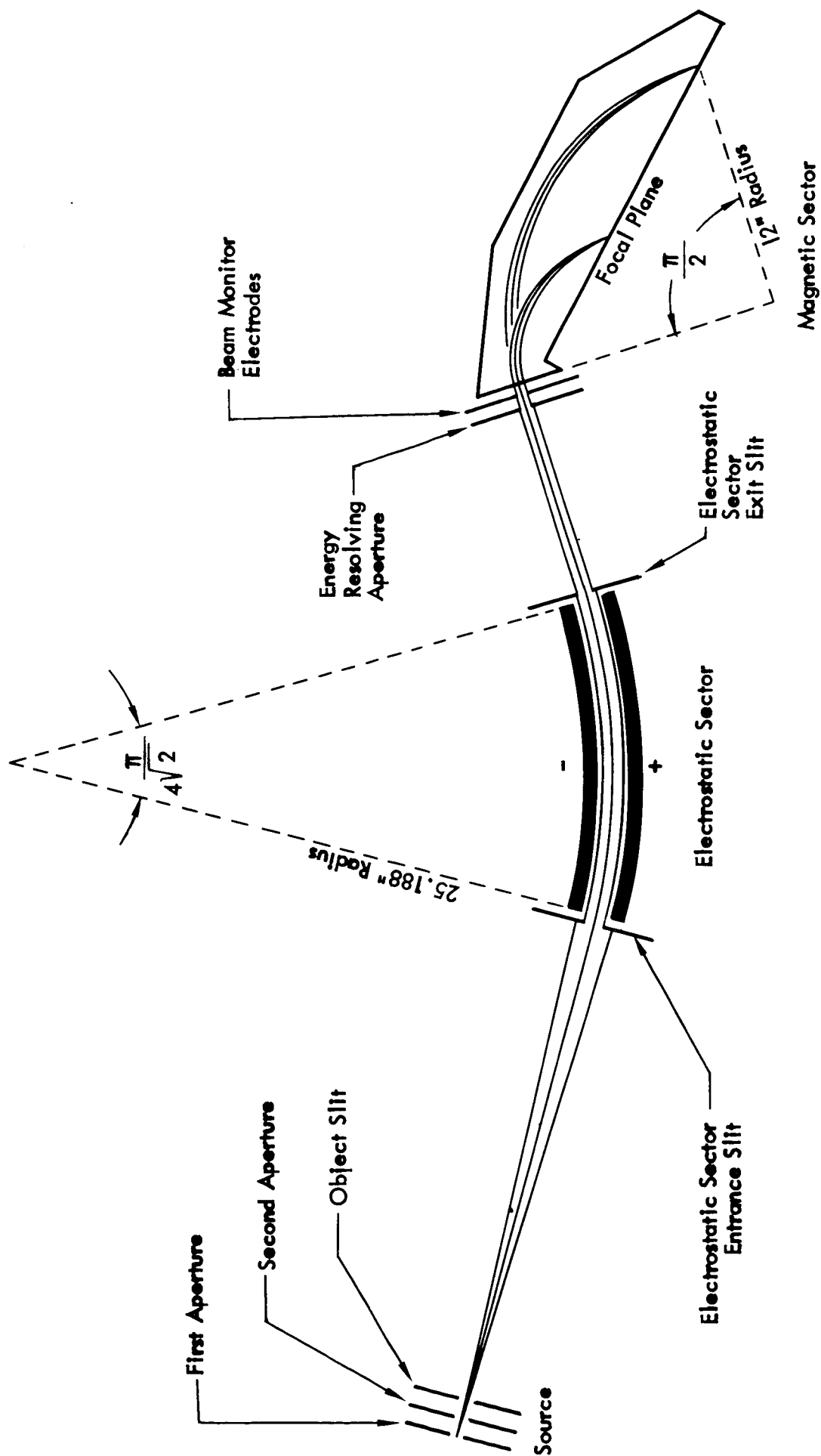


Figure 6-17: Mass Spectrometer Analyzer

different mass components. Each individual mass beam comes into focus at a different radius along the focal plane.

The velocity focusing feature of this analyzer makes it possible to alternate the focus from one mass to another rapidly by varying the accelerating potential of the ion beam. This eliminates the undesirable effects of hysteresis caused by varying the magnetic field. This capability is required for the quantitative analyses performed in this study.

6.4.2 Experimental Considerations

The experimental demonstration of the volatile metal chelate technique required several areas of effort: (1) preparation and characterization of standard chelates of the metals of interest, (2) determination of detection limits for the analysis with the mass spectrometer, (3) determination of the method for the formation of the metal chelate in the propellant, and (4) analysis of the test material remaining from previous demonstration testing.

Preparation of Metal Chelates - Some chelates of the metals of interest (including Fe, Cr, and Al) were available commercially in the hexafluoroacetylacetonate variety and were purchased from Pierce Chemical Company, Rockford, Illinois. However, chelates of the ligand heptafluorodimethyloctanedione, H(fod), which exhibited superior sensitivity with the mass spectrometer were not commercially available and had to be prepared in this laboratory. Fe(fod)_3 , Ni(fod)_2 , Ti(fod)_3 and V(fod)_3 were prepared according to the method given by Sievers, Connolly, and Ross⁽⁵⁹⁾. Cr(fod)_3 was prepared after the method of Springer, Sievers and Meek⁽⁶⁰⁾.

Tris (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato) iron (III), Fe(fod)_3

A 2.6 gram (8.8 mmoles) portion of H(fod) (Pierce Chemical Co.) was added drop-wise with stirring to a solution containing 1.364 grams (5.0 mmoles) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 150 ml of 95% Reagent alcohol (Baker). Water was added until two layers formed. The chelate was extracted with three -50 ml portions of hexane and the combined hexane extracts were washed with water. The hexane was removed under reduced pressure and

The resulting red crystals were sublimed at 90-100°C at reduced pressure. The first fraction sublimed was discarded. Dark red crystals of $\text{Fe}(\text{fod})_3$ were obtained

Bis(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)
nickel (II), $\text{Ni}(\text{fod})_2$

A .0115g (0.1 mmole) sample of nickel carbonate was moistened with 1 ml of CCl_4 . To this mixture was added 200 μl of $\text{H}(\text{fod})$. The mixture was warmed to 76°C for 10-15 minutes. The mixture was allowed to settle and samples for examination were drawn off the top of the liquid with a microsyringe.

Tris (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)
chromium (III), $\text{Cr}(\text{fod})_3$

An excess of chromium (III) nitrate nonahydrate (1.94 g., 5 mmoles) was dissolved in 30 ml of absolute ethanol. A solution of 4.4 g (1.5 mmoles) of $\text{H}(\text{fod})$ in 30 ml of absolute ethanol was added to the mixture and the mixture was warmed on steam bath for 20 minutes. The blue solution turned dark green. Water was added until two layers formed. The metal chelate was extracted with three - 50 ml portions of hexane. The combined hexane extract was washed with water. The hexane solvent was removed under reduced pressure yielding a dark green gummy solid. The solid was purified twice by sublimation giving dark purple crystals of $\text{Cr}(\text{fod})_3$.

Tris (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)
aluminum (III), $\text{Al}(\text{fod})_3$

A 1.87g (5.0 mmoles) sample of aluminum nitrate nonahydrate was dissolved in 30 ml of absolute ethanol. A solution of 4.4 g (1.5 mmoles) of $\text{H}(\text{fod})$ in 30 ml of ethanol was added to the mixture. The combined mixture was refluxed in a round bottom flask for one-half hour. Water was added and a white precipitate was formed. Hexane was added, forming two layers and dissolving the precipitate in the aqueous layer. The hexane layer was extracted and saved. The water layer was washed with two-20 ml portions of hexane which were added to the previous hexane portion. The hexane was evaporated with a stream of air and the yellow

solid product was sublimed at 100°C under reduced pressure. The first fraction sublimed was discarded. Sublimation was completed at 125°C and white crystals of Al(fod)_3 were obtained.

Tris (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)
titanium (III), Ti(fod)_3

Ti(fod)_3 was prepared in a micro reactor capsule by the direct action of H(fod) on titanium wire. A 1.60 mg sample of Ti wire from Alfa Inorganics (99.96% Ti) was placed in a 4 cm length of 2 mm glass tubing sealed on one end. 28 microliters (μl) of H(fod) and 2 μl of water were added to the tube. The contents were then cooled in liquid nitrogen and the open end was sealed. The tube was then heated at 170°C in an oil bath for four hours. The liquid color in the tube began changing from colorless to dark blue within 20 seconds after placing in the oil bath indicating the formation of Ti(fod)_3 .

Since titanium (III) complexes are rapidly oxidized in air (61,62), it was necessary to carry out subsequent operations in the nitrogen filled glove box. The reaction products in the glass tube were frozen in liquid nitrogen and the tube was opened at one end. The contents of the tube were washed into a 10 ml volumetric flask with degassed spectrophotometric grade acetone and diluted to the mark with acetone. The resulting solution was 1.6×10^{-4} g/ml Ti. The standard solution was then transferred to a serum-type bottle and sealed with sleeve-type, serum bottle stoppers. After the serum bottle was sealed, it was removed from the glove box.

Tris (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)
vanadium (III), V(fod)_3

V(fod)_3 was prepared in the same manner as the Ti(fod)_3 . A 1.70 g sample of vanadium wire (Alfa Inorganics, 99.98% V) was placed in a 4 cm length of melting point capillary tubing sealed at one end. 28 μl of H(fod) and 2 μl of water were added and the tube was sealed. The tube was then heated at 170°C in an oil bath for eight hours. The reaction between H(fod) and vanadium was somewhat slower than with titanium. In a few minutes, a slow color change to amber was noted. After a few hours, a color change to dark red was observed.

After the reaction was complete, the microtube was transferred to the glove box, the tube broken and the contents transferred to a 10 ml volumetric flask. After diluting to the mark with acetone, the contents were transferred to a serum bottle and sealed with a serum stopper.

The relative ease of oxidation of vanadium complexes is substantially less than that of titanium, but $\text{VO}(\text{x})_2$ complexes are known, thus, as a precaution against oxidation, $\text{V}(\text{fod})_3$ was excluded from air.

Bis (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)
manganese (II), $\text{Mn}(\text{fod})_2$

A small amount of $\text{Mn}(\text{fod})_2$ was prepared from 1.0 ml of Mn^{+2} solution (1000 ppm Mn) by evaporating to dryness and adding 100 μl of $\text{H}(\text{fod})$. Hexane was added and the mixture was warmed for 15 minutes. The resulting solution was diluted to 10 ml with pentane. No purification or isolation was attempted.

Mass Spectra of Metal Chelates - Mass spectra of the metal chelates used in this study were obtained using a DuPont 21-110B double-focusing mass spectrometer. The double-focusing feature greatly simplifies the quantitative analysis of the chelates. The standard operating conditions used were; source slit, 0.080 in., ionizing voltage, 70V; analyzer slit, .060 in.; and accelerating potential, 6KV. For spectra, the recorder was set to run at .08 inches per second and the magnetic scan rate was 5.0.

The metal chelates were introduced into the mass spectrometer through the direct insertion probe. Approximately one microgram of metal in the form of the chelate in a suitable organic solvent was used for each spectra. The solution was delivered to the glass capillary tube which fits into the end of the probe by means of a Hamilton microsyringe (10 μl capacity). With the probe at room temperature, the solvent was evaporated in the vacuum lock leaving the solid metal chelate in the probe tip. The probe was then inserted into the ion source where the chelate sublimed into the source. Figures 6-18 and 6-19 show the mass spectra of seven of the fod complexes prepared in this work. In general, the $\text{M}(\text{fod})_2^+$ peak was the most intense and was used for subsequent quantitative measurements. No importance should be given to the exact ratios

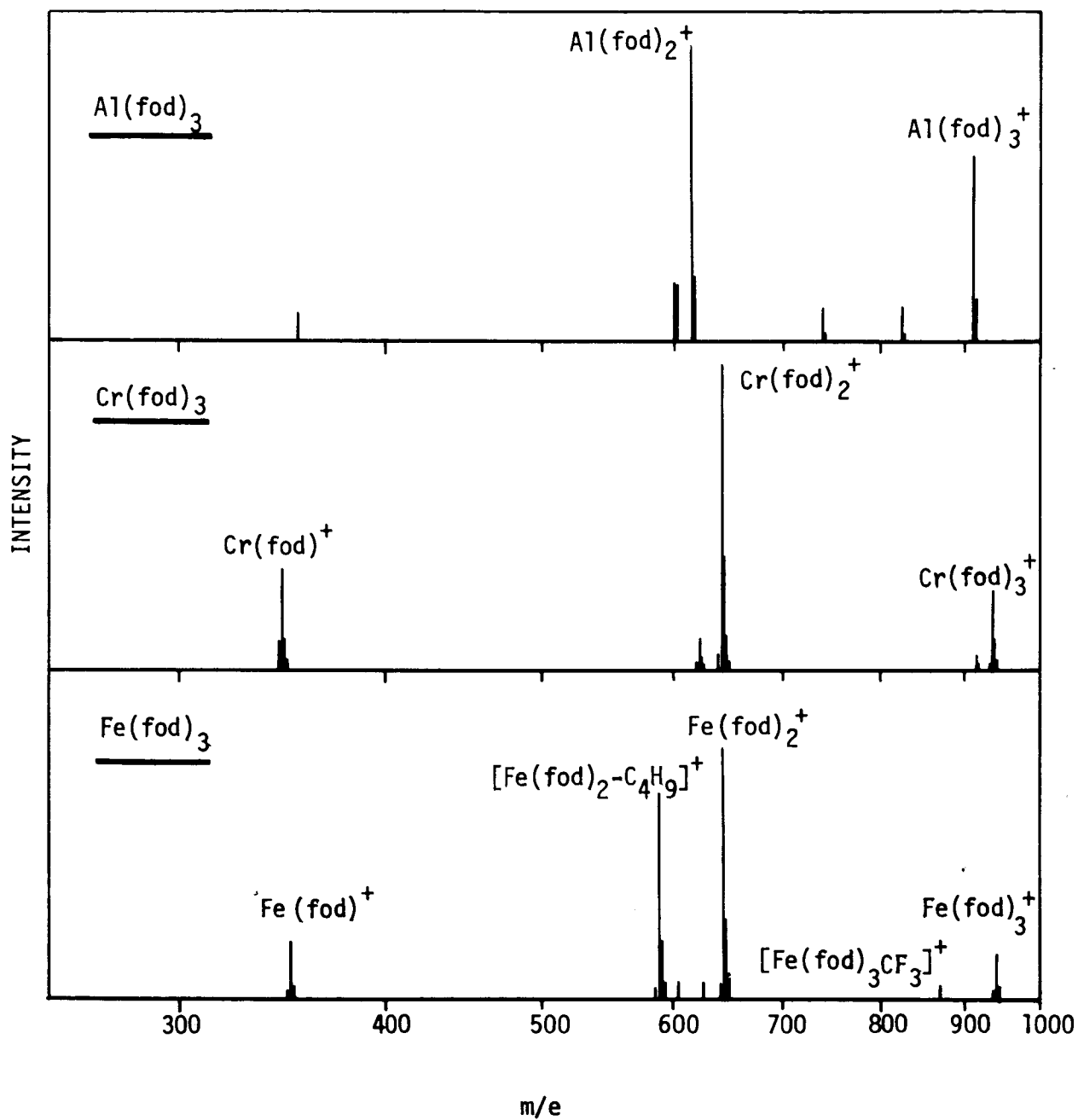


Figure 6-18: Mass Spectra of Al(fod)_3 , Cr(fod)_3 and Fe(fod)_3

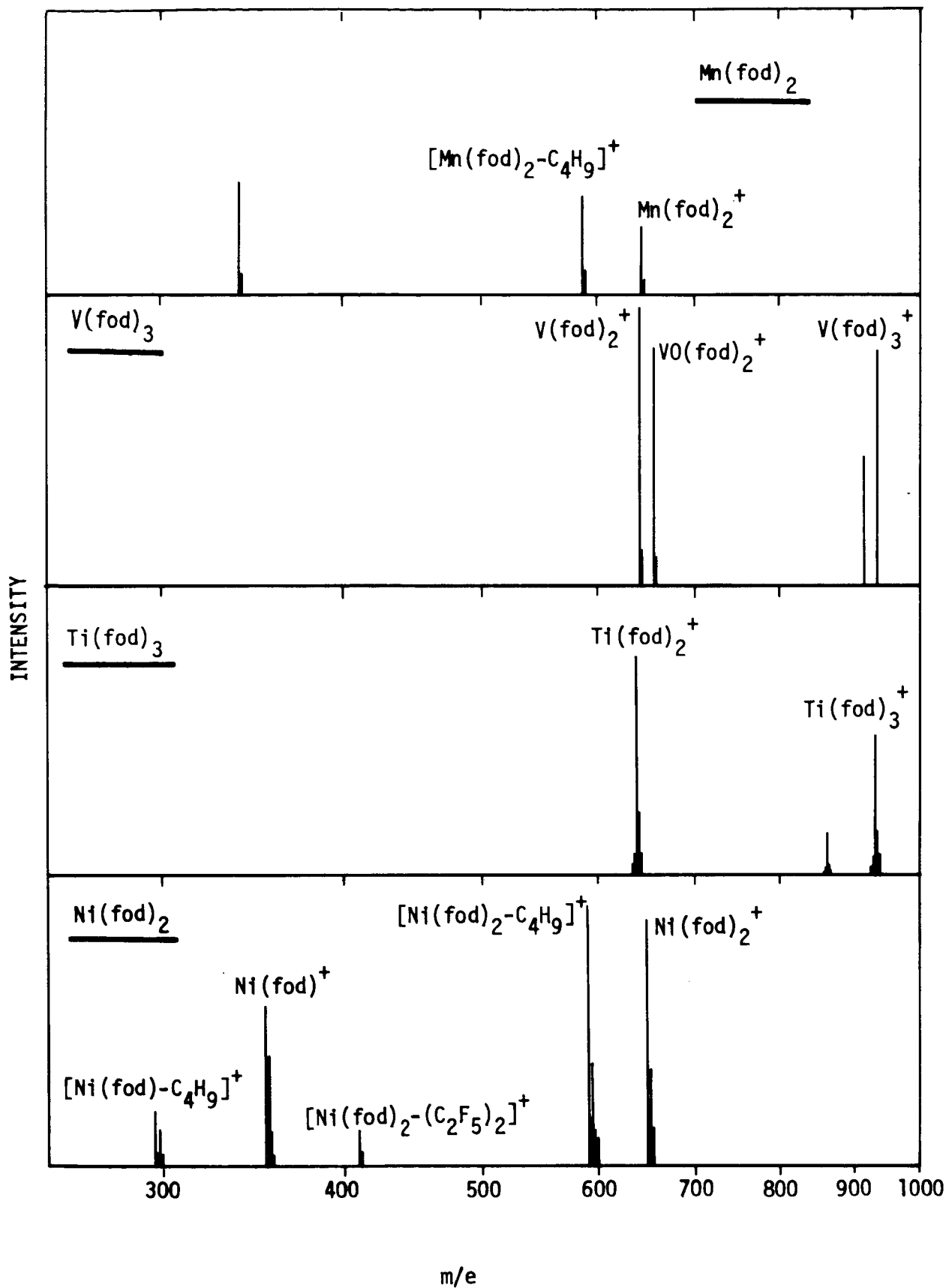


Figure 6-19: Mass Spectra of Mn(fod)_3 , V(fod)_3 , Ti(fod)_3 , and Ni(fod)_3

of one intensity to another in a single spectrum because the ion current was constantly changing as the compound vaporized into the ion source.

Quantitative Measurement of Metal Chelates Using the Mass

Spectrometer - The detector response at a given mass number is proportional to the concentration of the parent molecule in the ion source of the mass spectrometer. Through the use of appropriate standards and ordinary analytical techniques it is possible to perform quantitative analyses of volatile materials with the mass spectrometer.

Where the greatest sensitivity is required, the most intense mass peak is chosen for analysis. In the case of the tris metal chelates, the peak due to the $M(fod)_2^+$ fragment is the most intense. The desired peak is located by focusing the mass spectrometer on a reference mass peak of perfluorotributylamine (PFTBA) on the low mass setting and then setting the peak matching feature to give the proper mass number of the high mass.

With the mass spectrometer set to scan over the metal chelate peak at a rate of about one scan per second, the probe tip containing the chelate to be analyzed is inserted into the heated ion source. As the metal chelate volatilizes into the source, the appearance of the $M(fod)_2^+$ fragment is recorded on a strip chart recorder. Figure 6-20 shows a scan of the $Cr(fod)_2^+$ peak vs. time for a 1×10^{-10} g sample of Cr.

The detection limit in ppm for such an analysis can be determined from the following formula:

$$D.L. = \frac{M_{\min} F}{V} \times 10^6, \text{ ppm}$$

where M_{\min} is the minimum mass for which the mass spectrometer will give a response, F is the dilution factor that applies when preparing the chelates, and V is the volume of sample in ml that is used in the mass spectrometer. Thus, if 1×10^{-9} g Ti is the minimum detectable in the mass spectrometer, and if there was no dilution ($F=1$) and if the sample volume was 50×10^{-3} ml the detection limit for Ti becomes

$$D.L. = \frac{1 \times 10^{-9}}{.5 \times 10^{-1}} \times 10^6 = .02 \text{ ppm Ti.}$$

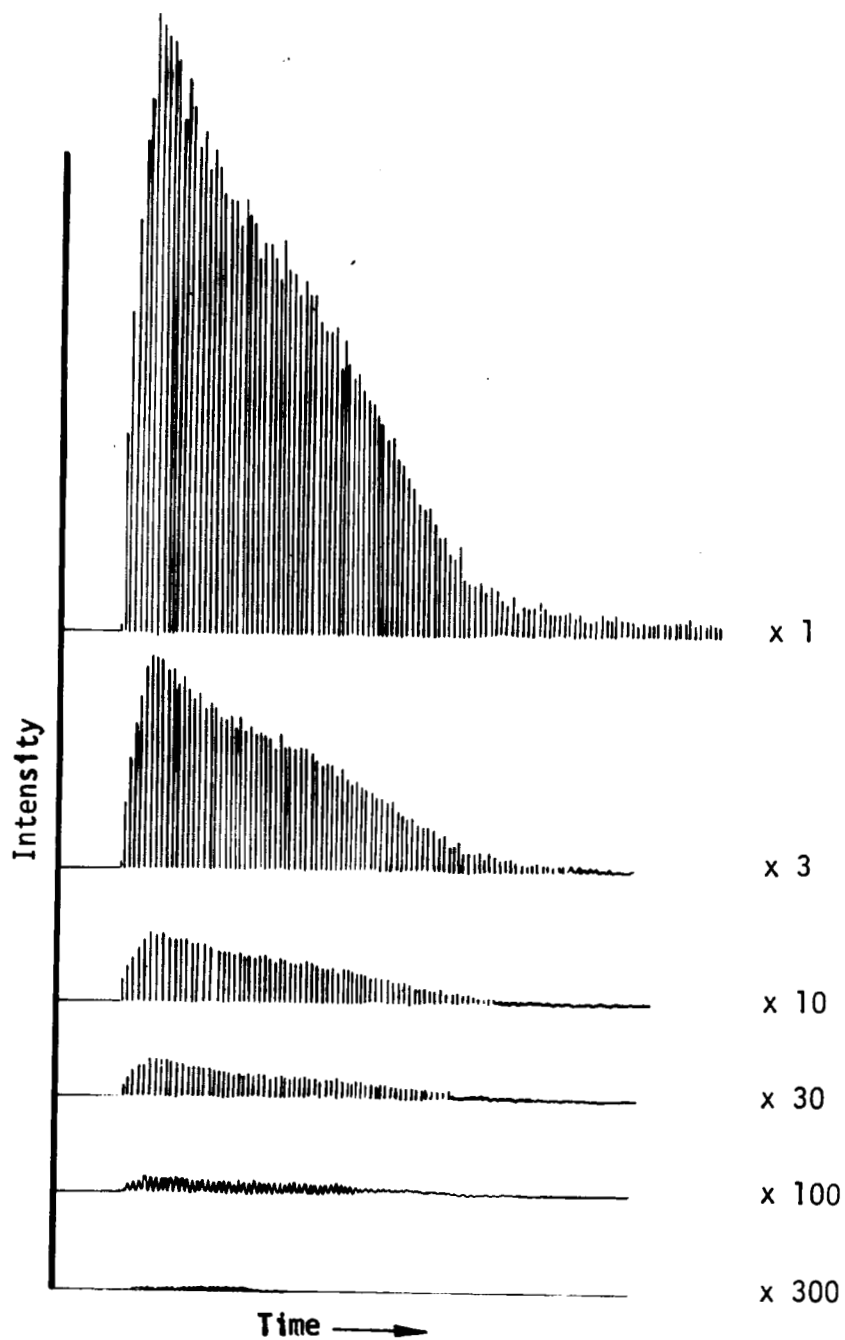


Figure 6-20: Time Resolved Recorder Trace for 1×10^{-10} g Cr as $\text{Cr}(\text{fod})_3$

It is evident that the detection limit is dependent on the sample volume used.

Analysis of Metals in Hydrazine - The material remaining from the experiment involving interaction between hydrazine and Type 304 corrosion resistant steel (Section 6.1) was analyzed for metal content using the volatile metal chelate technique. Considerable effort was devoted to insuring that quantitative chelation of the dissolved metals in the hydrazine was obtained.

At the completion of the previous experiment, the hydrazine was neutralized with hydrochloric acid and analyzed on the atomic absorption spectrometer (AAS) for trace metals. The resulting solutions were quite acid and required back neutralization with NaOH before proper reaction with the β -diketone could be obtained.

The general procedure used for analysis was: Pipette 1.0 ml of hydrazine solution into a 10 ml volumetric flask. Evaporate to dryness on a hot plate using a stream of air. Add NaOH in ethanol dropwise until basic to red litmus paper. Add ten drops 30% H_2O_2 . Evaporate the solution to dryness again. Add 50 microliters H(fod) and 1.0 ml hexane. Warm solution for 10-20 minutes at 70°C. Dilute with spectrophotometric grade pentane to the 10 ml mark.

Standards were prepared using aqueous solutions of known concentrations of metal ions according to the same procedure.

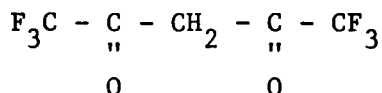
The metals in the hydrazine solution that were chelated were identified with the mass spectrometer and were measured according to the procedure outlined in the previous section. Sample size was varied to achieve the desired sensitivity.

Analysis of Metals in Oxygen Difluoride - There are two major problems involved in determining the metals dissolved or dispersed in liquid oxygen difluoride (OF_2) by the metal chelate technique: (1) OF_2 is highly reactive to most chemicals and (2) the OF_2 liquid region is -224 to -145°C. The first problem results in the reaction of the chelating agent (β -diketone or other types) with OF_2 instead of with the trace

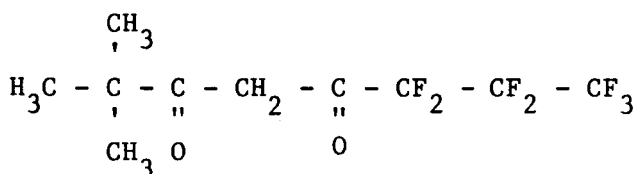
metals. If the first problem can be avoided, the second problem results in slow (or no) reaction with the β -diketone (solid at liquid OF_2 temperatures).

To evaluate these problems, small laboratory tests with liquid OF_2 were performed.

Two typical chelating agents were chosen for examination in OF_2 . One, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, was selected because its high degree of fluorination indicated that it might be stable in OF_2 . The other, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (H(fod)), was chosen because analysis involving metal chelates of this ligand have resulted in extremely low detection limits. It was reasoned that the highly fluorinated first compound, which shall be referred to as H(hfa),



would be resistant to further fluorination, whereas the H(fod)



which contains a hydrocarbon branch, might be attacked by OF_2 .

Determination of the relative stability of these two β -diketones was begun by placing .05 ml of the liquid compound in the bottom of a Pyrex glass tube fitted with a 10/30 standard taper joint. The Pyrex tube was then attached to a glass vacuum line that was used to transfer the OF_2 . The β -diketone was frozen with liquid nitrogen and the air in the tube was evacuated. The β -diketone was then allowed to warm to room temperature and OF_2 gas was introduced into each tube separately.

No apparent reaction was noted with the H(hfa) other than a slight increase in the yellow coloration of the liquid. The OF_2 was then condensed to the liquid state with liquid nitrogen. No change was noted after 15 minutes. The liquid nitrogen was removed and the OF_2 was permitted to warm and evaporate. A mass spectral analysis of the remaining material showed the presence of the parent molecule, H(hfa). No extraneous mass peaks were noted. Solid material on the walls of the

glass tube was noted in addition to the increase in yellow color. These observations indicate that some undefined reaction had taken place.

H(hfa) was judged suitable for limited contact with OF_2 .

Upon the introduction of gaseous OF_2 to the glass tube containing H(fod), the liquid H(fod) was observed to begin refluxing on the sides of the tube walls. Three to four seconds later a white flash was observed and the tube was violently blown off of the vacuum line. The identities of the reaction products were not determined. It was judged that H(fod) would not be suitable for use in direct contact with OF_2 .

Even though the compatibility problem can be solved through the use of H(hfa), the temperature problem (-145°C) was not solved. No reaction between H(hfa) and trace metals in OF_2 is possible at this temperature.

The appropriate way to establish metal concentrations in OF_2 is to allow the OF_2 to evaporate, leaving behind any metals or metal compounds and then treat the residue with the chelating agent desired. This avoids sticky problems of compatibility and allows reactions to be performed at room temperature or above. If the evaporation process is performed carefully, no loss of material in the OF_2 occurs.

For the demonstration of this technique, the material remaining from the dry activation analysis experiment (Section 6.2) was utilized. This also allowed a check between the two methods to be made. The OF_2 was in contact with 6061 aluminum for periods of time from six minutes to 5.4 hours.

The procedure used for analysis was as follows: To the polyvial containing the residue was added 0.1 ml of hydrofluoric acid solution. This converted any aluminum oxide to soluble aluminum fluoride. The inside surface was wetted with the HF solution. A 1.0 ml volume of distilled water was added to dilute the HF solution and the total contents were quantitatively transferred to a 10 ml volumetric flask. The polyvial was washed twice with 1.0 ml portions of water and the washings were added to the 10 ml flask. Ten drops of concentrated NaOH were added to the flask and the contents were evaporated to dryness under a stream of air. A small amount of hexane was added, along with 50 microliters of

H(fod) and the solution adjusted to a basic pH with NaOH in ethanol. The solution was heated to 70°C for 45 minutes and then diluted with pentane to 10 ml.

A standard aluminum fluoride solution was prepared from a weighed quantity of $\text{Al}(\text{OH})_3$ by treatment with HF solution. The AlF_3 solution was diluted to give a solution of 100 ppm Al^{+3} . Sample sizes of 10 to 100 microliters of the standard Al solution were treated according to the procedure above to prepare $\text{Al}(\text{fod})_3$ standards. A blank sample was prepared in the same way but with no AlF_3 solution added.

Analysis of Metals in Diborane - Section 6.3 reported the experiment wherein liquid diborane was stored in 6Al-4V titanium for a period of three months and the buildup of hydrogen from diborane decomposition noted. It is also significant to note whether or not any dissolution of the metal alloy occurred.

The problems involving the use of chelating agents in the presence of liquid diborane was similar to those involving OF_2 : diborane is highly reactive and has a very low boiling point. The solution to these problems was essentially the same also: evaporate the low boiling propellant leaving behind the impurities as a residue. It was not practical, however, to treat the residue in the titanium alloy vessel directly with the fluorinated β -diketone because of the danger of direct action of the β -diketone with the walls of the metal vessel. Thus a procedure of wiping the inside of the metal vessel with a moistened square of filter paper was instituted. This was relatively straightforward for the titanium vessel because the inside surface was machined smooth and the shortness of the vessel made all areas inside easily accessible. The titanium vessel to which foil had been added was not amenable to this procedure because the corrugations of the metal foil precluded quantitative removal of any residue.

The procedure used for the analysis was: Several one-inch squares of Whatman #40 ashless filter paper were moistened and used to wipe the inside area of the titanium vessel. The paper squares were collected in a 5 ml beaker. The following operations were performed in a nitrogen-filled glove box. Fifty microliters of H(fod) and 1.0 ml hexane were

added to the beaker and the contents were made basic to red litmus with a few drops of NaOH in ethanol. The contents were then warmed on a hot plate at 70°C for 30 minutes. The resulting solution was quantitatively transferred to a 10 ml volumetric flask. The beaker and filter paper was washed two times with degassed spectrophotometric grade pentane and the washings added to the flask. The solution was diluted to 10 ml and the contents were transferred to a serum bottle and sealed with a sleeve type serum stopper.

The above procedure was used for a blank with the exception that no wiping with the paper squares was done.

6.4.3 Results

Hydrazine - Type 304 Steel - The amounts of metals found in the hydrazine solution remaining from the experiment with stainless steel are recorded in Table 6-6. Iron and chromium were found in appreciable quantities, but the scope of the program did not permit a complete search for nickel, manganese, and cobalt. Since the original 15 ml volume of hydrazine was increased to 50 ml by neutralization for the atomic absorption analysis (Section 6.1.3), the concentrations of metals determined by the metal chelate technique was actually 15/50 times the value shown in Table 6-6. The values in the table correspond to 15 ml volume for comparison to the values reported for the radioactive tracer and atomic absorption technique results in Section 6.1.3. Thus the analysis was made well below the part-per-million level in the case of chromium.

The values reported for the sample S/V=1 by the metal chelate technique differ somewhat from the values reported by the radioactive tracer and AAS techniques. Although this discrepancy was researched, no satisfactory answer could be found. The other samples show satisfactory agreement considering the low level of concentration. It is plain that further study and technique refinements are necessary before this technique commands the consideration given atomic absorption spectroscopy.

Oxygen Difluoride - 6061 Aluminum - The sensitivity of the metal chelate technique toward detection of aluminum has been shown to be extremely high⁽⁵⁶⁾. This analysis has substantiated that previous finding. Indeed, the high sensitivity of detection of $\text{Al}(\text{fod})_3$ created

problems of background and contamination at the lower detection threshold. Fortunately, the material analyzed was substantially above the detection threshold.

The amount of metals dissolved or dispersed in OF_2 is shown in Table 6-7. The samples correspond to those reported in Section 6.2.3 in which 6061 aluminum foil was placed in contact with liquid OF_2 for periods of 6 minutes to 5.4 hours. With the exception of the first sample, the results agree well with the analysis given by neutron activation. It can be noted that while corrections to the neutron activation analysis results were necessary, the independent analysis by metal chelate techniques reinforces the validity of those corrections. No metal other than aluminum was detected in the mass spectra of the chelates of these samples.

Diborane - 6Al-4V Titanium - The analysis of the residue remaining after evaporation of the diborane from a 6Al-4V titanium vessel revealed that very little if any interaction takes place between diborane and titanium. The results of the analysis are shown in Table 6-8 and indicate that no detectable quantity of the major constituent, titanium, was taken up by the diborane. After subtracting the background (or blank), an extremely small amount of aluminum was noted, indicating that this element may be preferentially attacked in the alloy crystal lattice, albeit slowly.

The difficulty of analyzing titanium (oxidation problem) in no way detracted from the sensitivity possible with this technique. Detection of known quantities of $\text{Ti}(\text{fod})_3$ down to 1×10^{-9} grams was possible. Similarly, detection of $\text{V}(\text{fod})_3$ down to 3×10^{-11} grams was observed.

The extreme sensitivity of the $\text{Ti}(\text{III})$ complexes to oxidation was illustrated in the manner in which the $\text{Ti}(\text{fod})_3$ reacted with residual atmospheric oxygen during the analysis. In spite of rigorous precautions to keep the $\text{Ti}(\text{fod})_3$ from all air (e.g., the glove box atmosphere was provided by the boiloff from liquid nitrogen (typically 1 ppm O_2), solvents were degassed by freezing and thawing three times in vacuum, and the $\text{Ti}(\text{fod})_3$ solutions were sealed in serum bottles), the slow color change from dark blue through green to amber testified to the fact that some of the $\text{Ti}(\text{fod})_3$ was being converted to $\text{TiO}(\text{fod})_2$. Fry and Watt⁽⁶²⁾ reported pure $\text{TiO}(\text{fod})_2$ to be yellow in color. Consequently, it was

Table 6-6 METAL CONCENTRATIONS IN HYDRAZINE

<u>Sample</u>	<u>Metal</u>	<u>Metal Chelate</u> ppm	<u>Radioactive</u> <u>Tracer, ppm</u>	<u>Atomic Absorption</u> ppm
S/V = 1	Fe	180.	66.3	75.4
	Cr	1.3	30.5	23.8
S/V = 11	Fe	60.	50.9	45.6
	Cr	17.	17.5	12.2
S/V = 56	Fe	13.	12.7	8.6
	Cr	1.0	4.4	3.5

Table 6-7 METAL CONCENTRATIONS IN OXYGEN DIFLUORIDE

<u>Sample</u>	<u>Metal</u>	<u>Metal Chelate</u> ppm	<u>Neutron Activation</u> ppm
A1-1	Al	2.3	.68
A1-2	Al	.14	.25
A1-3	Al	1.3	1.0

Table 6-8 METAL CONCENTRATIONS IN DIBORANE

<u>Sample</u>	<u>Metal</u>	<u>Metal Chelate</u> ppm
6Al-4V Ti Vessel	Ti	< .02
	Al	.09
	V	< .0008

necessary to prepare the Ti(fod)_3 and subject it to mass spectral analysis the same day. Identical procedures were followed in the analysis of both standards and unknowns in so far as possible.

A comment on the difference in detection limit of the metal chelate in mass spectrometer and to what limit that corresponds in the original sample is in order. The mass spectrometer by its nature, is limited to extremely small samples. If the sample size is not maintained within reasonable upper limits, the vacuum in the mass spectrometer plumbing is upset and a loss of sensitivity and resolution results. Consequently, samples for direct introduction into the ion source are generally limited to a few micrograms or less. Sample volumes from 1 to 10 microliters are typically employed and the solvent is pumped away, leaving a minute amount of solid. This 1 μl sample was typically obtained from a total solution of 10 ml volume which was made up from a 1 ml original sample. This means that a dilution factor of as much as 10^5 applies, so that an original sample concentration of 1 ppm ($\sim 1 \mu\text{g/ml}$) may yield a sample weight of as little as 1×10^{-10} grams at the mass spectrometer inlet. This presents no problem for the more sensitive compounds such as Al(fod)_3 , but for detection compounds having less sensitivity, detection below 1 ppm concentration level may prove difficult. The above dilution factor represents the results of typical experimental procedures and with a little effort the value could be decreased so that more of the original sample gets to the mass spectrometer for analysis. Explicitly, a larger than 1 ml volume sample could be used, the chelate solution could possibly be limited to 1 ml or less, and direct introduction sample sizes may be increased to 50 or 100 μl total by pumping the solvent off several times and adding more sample (the sample holder is generally limited to 20 μl).

Stability of the Metal Chelates - Kowalski, Isenhour and Sievers⁽⁶³⁾ reported that the metal chelates of H(fod) were quite stable in pentane, but showed a tendency to decompose in acetone. In this work, hexane was used in addition to pentane and acetone. Observation of the solutions and mass spectra confirmed the findings of Kowalski. The metal chelates were stable for an indefinite period in hexane or pentane, while decomposition was noted in acetone. For the case of Ti(fod)_3 in acetone,

decomposition was evidenced by a color change from light amber to a dark red solution. Hexane and pentane were preferable solvents for an additional reason: they were quickly removed in the vacuum lock, with pentane being the more rapid. Acetone takes substantially longer than pentane.

In the solid (crystalline) form, the metal chelates appear to be stable indefinitely (with the exception of those subject to oxidation), although they should be stored in a desiccator to avoid hydration.

Accuracy of the Quantitative Measurements - It is interesting to compare the accuracy of the metal chelate technique with other proven methods, such as atomic absorption spectroscopy and neutron activation. Such a comparison is shown in Table 6-9.

Table 6-9 COMPARISON OF THE ACCURACY OF THE VOLATILE METAL CHELATE, ATOMIC ABSORPTION, AND NUCLEAR ACTIVATION TECHNIQUES

Technique	Accuracy
Volatile Metal Chelate	5 - 10%
Atomic Absorption	Iron 2% Aluminum 5%
Nuclear Activation	Variable, 1 to 0.1% depending on counting statistics

The two main limiting factors to the accuracy of the metal chelate technique are the reproducibility of sample size into the mass spectrometer and the reproducibility of the vaporization process in the ion source. A 10 μ l microsyringe is used to deliver samples to the direct insertion probe and is calibrated in divisions of 0.5 μ l. This is approximately the limit to which one can reproducibly deliver samples. Consequently it is better to use a full syringe for a sample than to use only 10% of the syringe volume. The reproducibility of the vaporization process is somewhat more difficult to control. The temperature of the ion source and probe heater should be held constant and the time from initiation of solvent pump-off to probe insertion should be constant.

Several other possible sources of error should be pointed out. The rate of solvent pump-off in the vacuum lock should be slow and controlled to avoid spattering and loss of sample in the lock. The probe tip should be well cooled between successive analyses to avoid chelate sublimation in the vacuum lock and subsequent erroneous results. Finally, the oxidation of $M(\text{fod})_3$ complexes to $MO(\text{fod})_2$ compounds alters the results for those chelates that are susceptible to atmospheric oxidation.

7.0 CONCLUSIONS

The search for techniques which would allow qualification of materials for long term use with liquid propellants in spacecraft in a very short time yielded a number of techniques which met the program requirements. These were

1. radioactive tracer
2. neutron activation
3. palladium foil hydrogen analyzer
4. volatile metal chelate
5. atomic absorption spectroscopy

The first four of these techniques were chosen for technical demonstration. It was concluded that these techniques can distinguish between gross and subtle effects of compatibility and can produce data in a short time.

The radioactive tracer technique was well suited to following the rate of interaction between a selected metal material and a liquid propellant. The demonstration of this technique using radioactive Type 304 corrosion resistant steel and liquid hydrazine yielded data about the metal uptake by hydrazine that heretofore had never been generated. The data showed a continual increase in the concentrations of iron and chromium as a function of time over a period of seven months. The concentrations of these metals as a function of surface area at constant time were not as expected, however. It was felt that certain, as yet unidentified, contaminants and/or variables in the hydrazine could account for the anomalies observed.

The neutron activation analysis technique was best suited to trace metals where a "one time," test point would be satisfactory. For some metals, neutron activation analysis had the highest sensitivity of any technique tested (Mn, .000004 ppm). It was concluded that activation analysis was developed to the point that routine analyses can be performed at a reasonable cost. The use of activation analysis for the determination of metals dissolved or dispersed in liquid OF_2 when stored

in 6061 aluminum was considered conditionally successful. A problem of aluminum contamination from the nuclear reactor made accurate analysis of the extremely low level of aluminum difficult. It was concluded that this problem could be overcome by careful use of new/clean containers.

The use of the palladium foil hydrogen analyzer (PFHA) to determine hydrogen build-up over liquid diborane was very successful. The measurement of minute amounts of hydrogen (1×10^{-7} grams) indicated that very little interaction between diborane and the metal containers was taking place. It was concluded that the PFHA was a valuable tool in establishing material-propellant functional performance on a relative basis. For instance, in the order of increasing hydrogen build-up over diborane were the metals:

304 steel < 6061 aluminum < 6Al-4V titanium.

The use of volatile metal chelates and mass spectrometer to determine trace metals in liquid propellants was demonstrated successfully. The technique proved to be very sensitive to aluminum and chromium (aluminum sensitivity, .00002 ppm), being better than activation analysis for these metals. Results obtained for the metals in liquid hydrazine agreed well with other analytical techniques. Good agreement was also obtained with this technique compared to neutron activation for the metals dissolved in liquid oxygen difluoride. The method showed that no measurable quantity (less than .02 ppm) of titanium was taken up from a 6Al-4V titanium vessel by liquid diborane at -230°F , although a trace of aluminum was found. It was concluded that the metal chelate technique qualified for consideration as an advanced technique but that further development work was required to make it valuable as a routine analytical method.

It should be noted that none of the demonstration experiments made any attempt to simulate the zero-g environment of space. Such simulation may prove to be especially difficult and expensive. Complete quiescent testing may be the best way to approach this simulation. At the very low concentrations of contaminants encountered, however, no substantial difference between the quiescent and agitated testing would be expected.

8.0 RECOMMENDATIONS

The anomalies observed in the hydrazine-stainless steel demonstration test point out the need for additional study of that system. The tests have shown a steady increase in iron and chromium in the hydrazine but also an apparent independence of the build-up to material wetted surface area (refer to data in Section 6.1.3, pages 51 to 53 showing essentially the same metal concentrations for all surface areas). Possibly some other rate controlling factor (such as water concentration) was obscuring any surface controlled reactions. This reaction mechanism problem can be effectively studied using the radioactive tracer technique and reliable kinetic rate data can be generated. The need for such studies and data is substantiated by extrapolation of present data, which indicates that after ten years exposure to stainless steel, hydrazine could be expected to contain about 1000 ppm each of iron and chromium.

Studies with varying amounts of impurities found in hydrazine (such as water, aniline, and carbon dioxide) are recommended to isolate the rate controlling factor(s) for the reaction. Knowledge of these rate controlling factors would then provide a means of eliminating any metal build-up problem (i.e., by reducing the concentration of the rate-controlling substrate). Knowledge of the controlling kinetics would also provide a means to correlate short term data to long term interaction.

Considering the promising aspects of the volatile metal chelate technique, further study and application of this method are recommended. The high sensitivity and specificity of the technique rival the neutron activation analysis technique yet is not hindered by half-life problems. The ability to analyze complex samples make it a natural choice when working with metal alloys with more than one major component (such as steel).

Two other techniques worthy of further investigation were reviewed which may meet the program requirements but were not demonstrated. One, the anodic stripping electrochemical technique, is reportedly extremely

sensitive; the other, a surface impedance measurement, looks very promising, but its sensitivity and practical utility have not been established. It is recommended that these two techniques be investigated further.

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